

A HOLISTIC APPROACH TO SAFETY ASSESSMENT IN THE LIFE CYCLE OF BIODIESEL INDUSTRY

A Thesis

by

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ABSTRACT

A number of goals have been set in several countries to rapidly increase biofuels production and focus more on sustainable energy resources because of limited fossil fuel reserves versus renewable biofuels, global warming and climate change. Biodiesel considers very attractive environmentally friendly fuel because it is compatible with the existing diesel engines with little or no modification needed. The majority of the studies performed to improve the biofuel industry was done from economic, environmental or social point of view but failed to include the safety aspects in the whole analysis. In this thesis, a holistic approach is presented to conduct a life-cycle assessment of the risks associated with the supply, transportation, processing, storage, and production of biomass to biodiesel by assessing technologies and supply chains. Total risk calculations were done quantitatively and semi-quantitatively utilizing the historical record of the reported accidents/incidents from 2006 to 2013 in the United States. Based on the work done in this thesis, several key results were obtained. It was found that fire in biodiesel plants accounts for the most likely scenario for an accident (around 85% of total accidents). It was also found that the process area contributed the highest percentage of accidents (43%) followed by storage (33%). In the transportation phase, the overwhelming majority of events (98%) occurred as a result of spillage. In general, the thesis results demonstrate that assessing the risk utilizing the real accident scenarios to know the safety trend involved can be utilized afterwards to anticipate the upcoming loss from the capacity increase. The results also provide further evidence on the effectiveness of the use of overall risk

calculations to get better understanding of the incident situations, facilitate more organized and successful emergency response, highlight the areas that need more attention and improvement, and more importantly act towards a life-cycle approach that is aimed at keeping overall risk within acceptable limits. The thesis analyzes reported data and discusses root causes and potential mitigation strategies.

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1. INTRODUCTION

There is a global trend to reduce the dependence on dwindling fossil fuels by utilizing sustainable energy resources. One of these resources is biofuel that gained very strong attention in the last few decades. The term biofuel refers to biomass-based liquid, gas or solid that can be classified into two main categories: primary biofuels and secondary biofuels. Primary biofuels are used in natural or unprocessed form for heating, cooking, electricity production such as fuel wood, wood chips, pellets, etc. While, Secondary biofuels are produced by the biomass processing; such as bioethanol, biomethanol, biodiesel, bio-oil, biohydrogen, syngas, etc. The Secondary biofuels are often categorized into first, second, and third generations based on the type of raw materials involved and the applied conversion mechanisms or process technologies (Nigam and Singh, 2011).

There are several significant benefits from developing biofuels in large scale. Some of them are limited fossil fuel reserves versus renewable biofuels, ease of availability of raw materials (agricultural, aquatic or even recycled sources), simplicity of production methods, flexibility of different capacities of Biofuels comparing to petroleum-based fuels, global warming and climate change, eco-friendly alternative since it reduces GHG emissions and produces far less air pollution than conventional diesel fuel or petrol (Naik et al., 2010; Nigam and Singh, 2011).

Further, a number of goals have been set in several countries to rapidly increase the production of biofuels, among them the European Union that's mandated 10% of all transportation fuels to be used from biofuels by 2020 (Nigam and Singh, 2011) and the United States that set a near-term goal of a 20% reduction of gasoline usage in 2007- by producing more biofuels- to be achieved by 2017, as well as a long-term goal to replace 30% of gasoline demand in 2006 by 2030 (Foust et al., 2009). Therefore, biodiesel production has been increasing over the last few years worldwide (EPI, 2012; REN21, 2014) and within the United States (EIA, 2014d), as shown in **Fig. 1.1**.

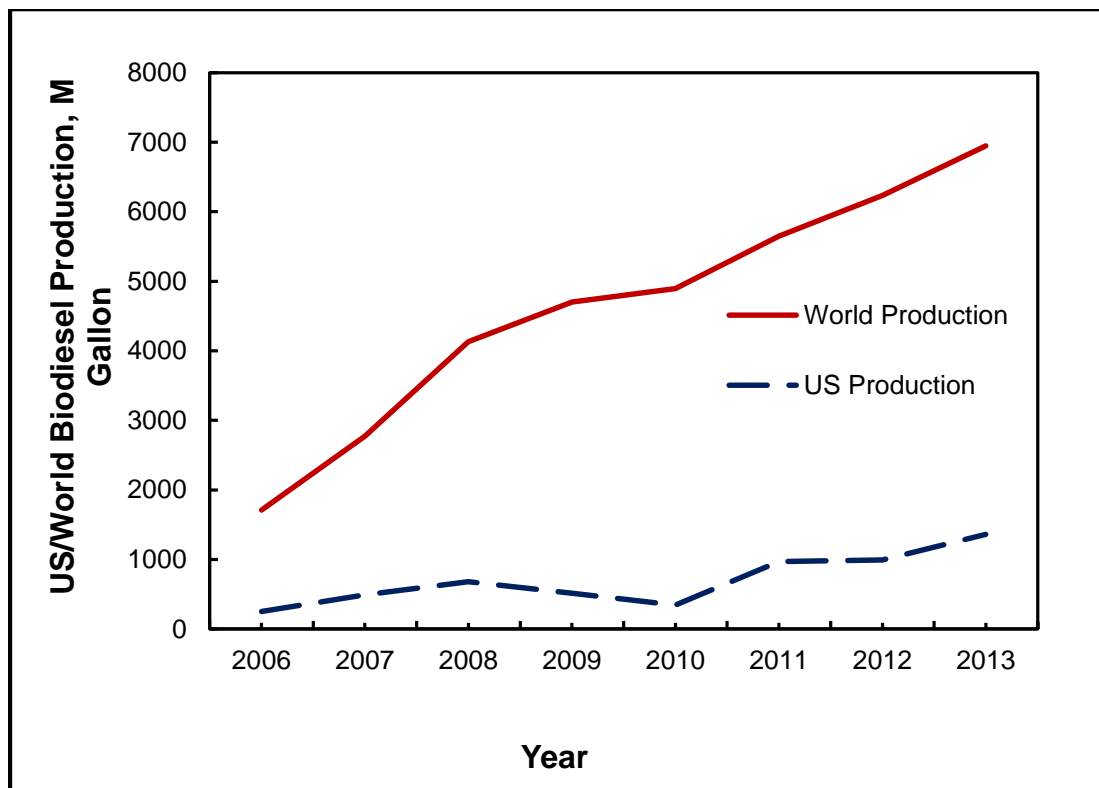


Fig. 1.1: World and US biodiesel production over the period between 2006 and 2013.

Biodiesel as a biofuel was very attractive though because its chemical structure and energy content are very close to the conventional diesel fuel, which in turn make it compatible with the existing diesel engines with little or no required modification. Biodiesel can be produced through at least four ways; direct use and blending, micro-emulsion, thermal cracking (pyrolysis), and transesterification. Among the previously mentioned ways, transesterification can be considered as the most popular method. In transesterification, a reaction of triglyceride, such as vegetable oil or animal fats, take place with an alcohol in presence of a catalyst to produce fatty acid esters (biodiesel) and glycerol. Several alcohols can be used such as methanol, ethanol, propanol, butanol, etc. and various catalysts are reported whether they are acidic, alkaline, or enzymatic (Yusuf et al., 2011).

As biodiesel is a relatively new industry, new technologies operated by new unskilled/semiskilled operators come into sight. Along with many companies want to change from fossil to bio-feedstock/fuels without develop adequate petroleum-replaced strategies. Moreover, the process of building and operating of these bio-refineries/Bio-fuel process plants was done in potentially inappropriate locations; for instance near large populations. By analyzing the reasons behind the reported accidents, it appears that with increasing the biofuel production so rapidly in the recent decades; there is a huge rise in the number of bio-refineries which in turn increases the risk and more accidents occur. From the statistics that have been reported for accidents in bioethanol and biodiesel industries, it can be concluded that about six fires and explosion incidents are reported every year in the United States alone (Nair, 2010).

1.1 Thesis Overview

The rest of the thesis will follow the structure outlined below. Section 2 services as an introduction to the biodiesel industry, methods of processing and production, risk in biodiesel plants, and the concept of life cycle assessment which was applied in this study.

Section 3 describes the problem statement, the methodology, and the approach used to address the risk assessment in the biodiesel industry in the United States over the period between 2006 and 2013.

Section 4 discusses the data collected for the accidents in biodiesel plants and how the data was used to determine the quantitative risk and construct a safety matrix for biodiesel plants.

Section 5, following the same approach, accident data in the biodiesel transportation were used to determine the risk over the period under investigation (2006-2013) in both quantitative and semi-quantitative ways.

In section 6, the data from the previous two sections were combined to determine the overall risk and construct an overall risk matrix that describe the risk levels in biodiesel industry based on both phases (plant production and transportation).

Conclusions and ideas for expanding the current work are discussed in section 7.

2. BACKGROUND AND LITERATURE SURVEY

This section is intended to explain more about the overview of biodiesel industry, methods of processing and production, risk in biodiesel plants, and the concept of life cycle assessment that was applied in this study.

2.1 Biodiesel Overview

After the oil crises occurred in 1970's -1980's, there has been a huge debate about the limitations of world oil supply and fossil fuels depletion. These concerns raise legitimate discussion on energy security. Additionally, fuel prices had a boost in the mid-2000's which in turn has encouraged many countries to use alternative energy sources as shown in **Fig. 2.1**, (Atabani et al., 2012). The primary energy consumption of the United States alone in 2010 was about 98 quadrillion Btu (quads) which approximately equals 19% of world total primary energy consumption, 511 quads, at that time (EIA, 2014b).

In 2013, the total U.S. energy production approached 81.7 quads which were just sufficient for 84% of total U.S. energy demand (97.5 quads). In the same year, 82% of United States total consumption was from fossil fuels, 10% from renewables, and 8% from nuclear energy as shown in **Fig. 2.2** (EIA, 2014e).

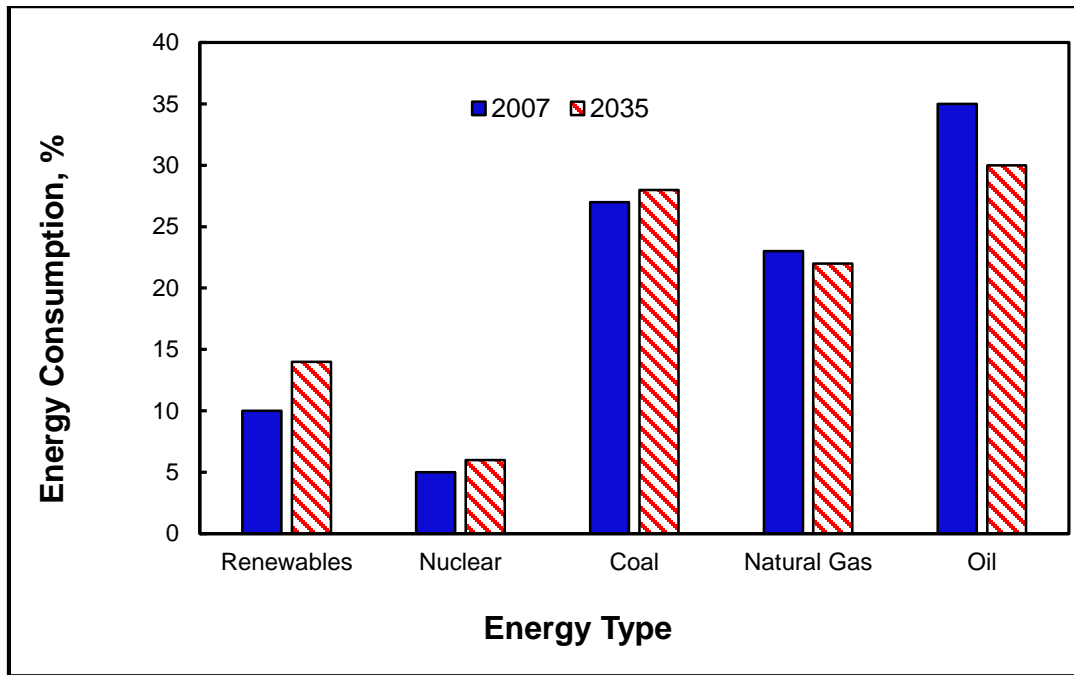


Fig. 2.1: World energy consumption by fuel type in 2007 and 2035 (Data modified from Atabani et al., 2012).

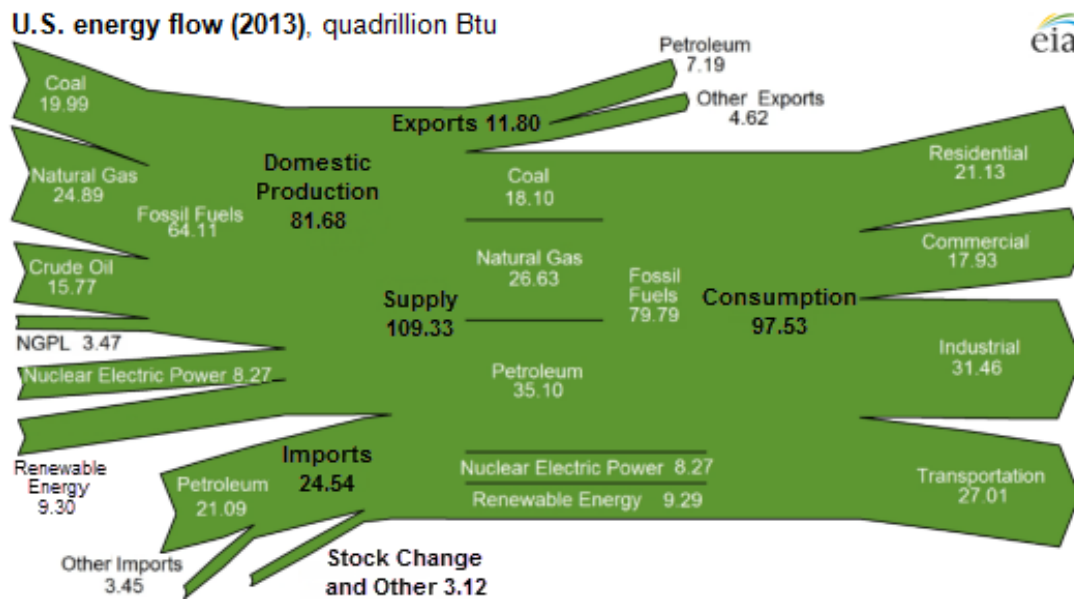


Fig. 2.2: U.S. energy flow 2013 (EIA, 2014e).

Among many renewable fuels, biodiesel has been receiving attention due to several advantages of its use. Biodiesel is biodegradable; it degrades nearly four times faster than petro-diesel. Biodiesel has 10–11% of oxygen; though it has high combustion characteristics and its oxygen content improves and accelerates the biodegradation process. Biodiesel is sustainable, environmentally friendly and free from sulfur and aromatic content whereas petro-diesel can contain up to 500 ppm SO₂ and 20–40 wt% aromatic compounds. Biodiesel also reduces net carbon-dioxide emissions by 78% on a lifecycle basis when contrasted with petro-diesel and lessens smoke because of its free soot. It decreases dramatically engine exhaust emissions when combusted as carbon monoxide (CO) emissions by 46.7%, particulate matter emissions by 66.7% and unburned hydrocarbons by 45.2% compared to petro-diesel. It is non-toxic which makes it beneficial for transportation in very critical environments as marine ecosystems and mining enclosures. It is non-flammable and has a higher flash point (above 100–170 °C) than petroleum diesel (60–80 °C). Biodiesel has higher cetane number (about 60–65 based on the vegetable oil used) than petro-diesel (53) which in turn decreases the ignition delay. Biodiesel has excellent lubricant properties compared to very-low-sulfur diesel which in turn improves lubrication in fuel pumps and injection system and decreases engine wear, tear and increases engine efficiency. Biodiesel may not need engine modification up to B20 while higher blends may require some minor modification and it can be made out of recycled waste cooking oils and lards which reduces the environmental effect of a waste disposal of such oils and fats (Phan and Phan, 2008; Helwani et al., 2009; Yusuf et al., 2011; Atabani et al., 2012).

There are different types of oils and fats that can be used as feedstocks for biodiesel production. Examples are edible oils as oils extracted from soybeans, rapeseed, safflower, rice bran oil, barley, sesame, groundnut, sorghum, wheat, corn, coconut, canola, peanut, palm and sunflower. Non-edible oils include waste or recycled oils and fats, jatropha curcas, mahua, pongamia, camelina, cotton seed, karanja or honge, cumaru, and jojoba. Also, Animal fats can be used as pork lard, beef tallow, poultry fat, fish oil and chicken fat. And other sources also have been reported as bacteria, algae, microalgae, tarpenes poplar, switchgrass, miscanthus, latexes and fungi (Atabani et al., 2012).

As can be concluded from the US Energy Information Administration (EIA) Monthly Biodiesel Production Report (EIA, 2014c), biodiesel is produced from numerous types of oils and fats. From them it appears that soybean oil is accounted for more than 50% in 2013 while recycled waste cooking oil and grease accounted for a little more than 10% in 2013 as can be depicted from **Fig. 2.3**.

Choosing the cheapest feedstock is essential to assure that biodiesel production cost is economical. It was determined that the soybean oil studied as a feedstock was accounted for more than 90% of the total annualized cost of biodiesel production (Myint and El-Halwagi, 2009). While in other literature, it has been found that generally feedstock alone represents around 75% of the overall production cost of biodiesel as illustrated in **Fig. 2.4** (Atabani et al., 2012).

Major biodiesel feedstocks (2013)

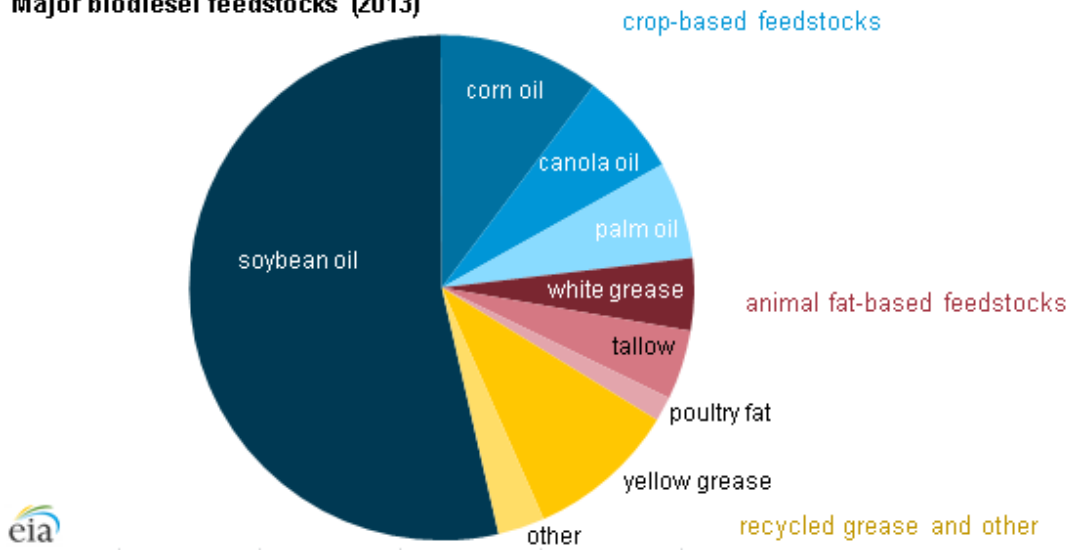


Fig. 2.3: U.S. major biodiesel feedstocks in 2013 (EIA, 2014c).

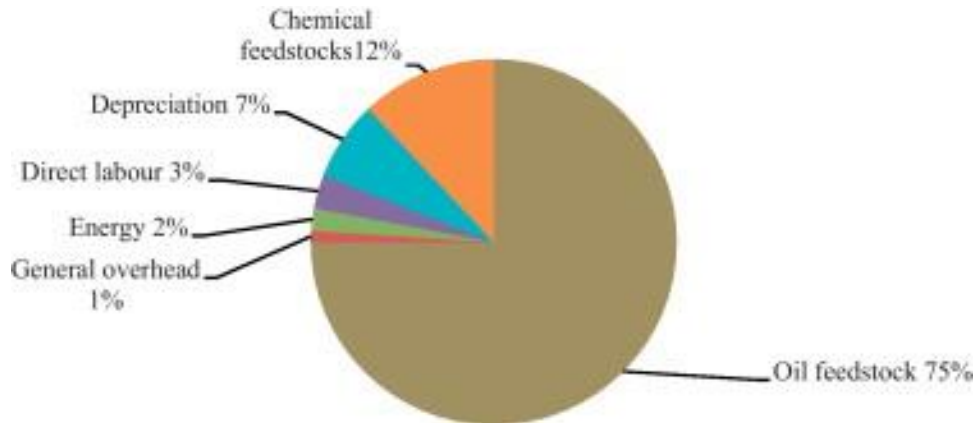


Fig. 2.4: A representation of overall production cost of biodiesel (Atabani et al., 2012).

USDA, Economic Research Service recently released studies in U.S. Bioenergy Statistics (USDA, 2014b) and Oil Crops Outlook (USDA, 2014a) regarding common biodiesel feedstocks as oils/fats supplies and prices as well as a comparison of average monthly prices (\$/gallon) of Blend 100% biodiesel (B-100) as a Soy methyl ester free on board (FOB) price at IL, IN and OH and On-highway average diesel price as shown in **Fig. 2.5** through **Fig. 2.7**.

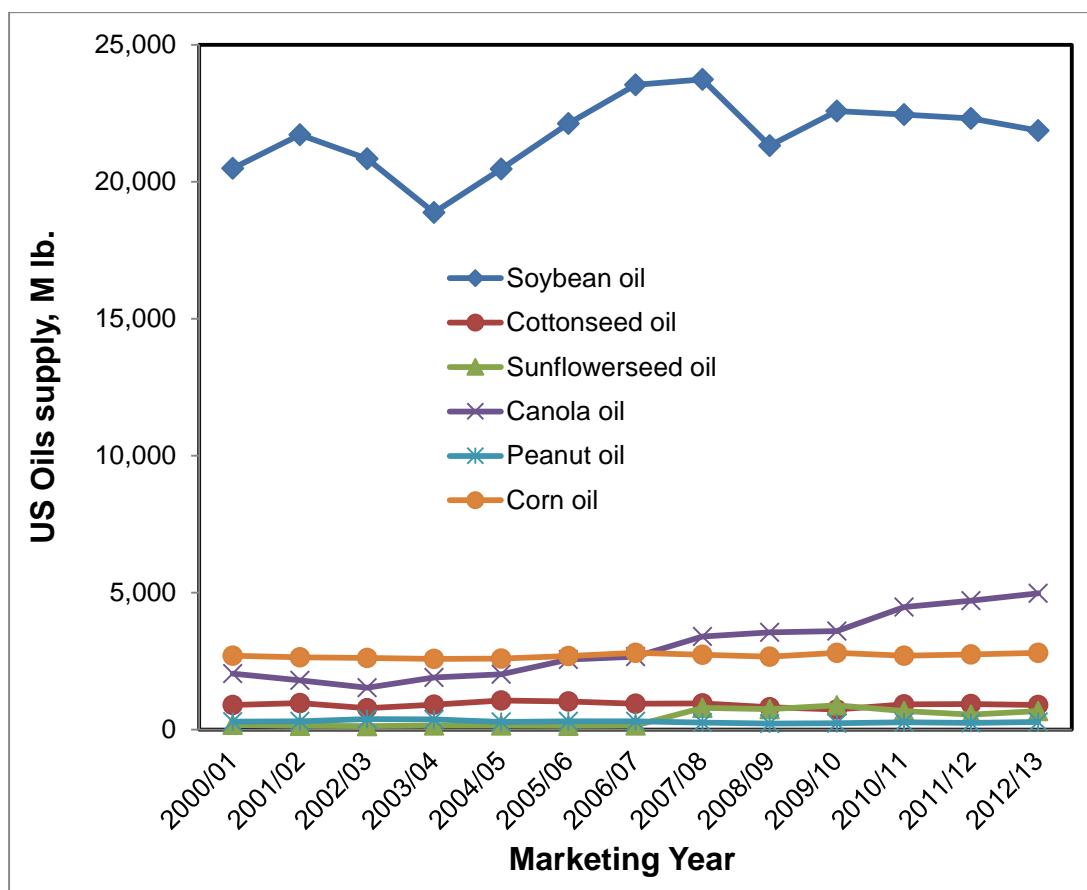


Fig. 2.5: U.S. annual oils supply from 2000 till 2013 (USDA, 2014a).

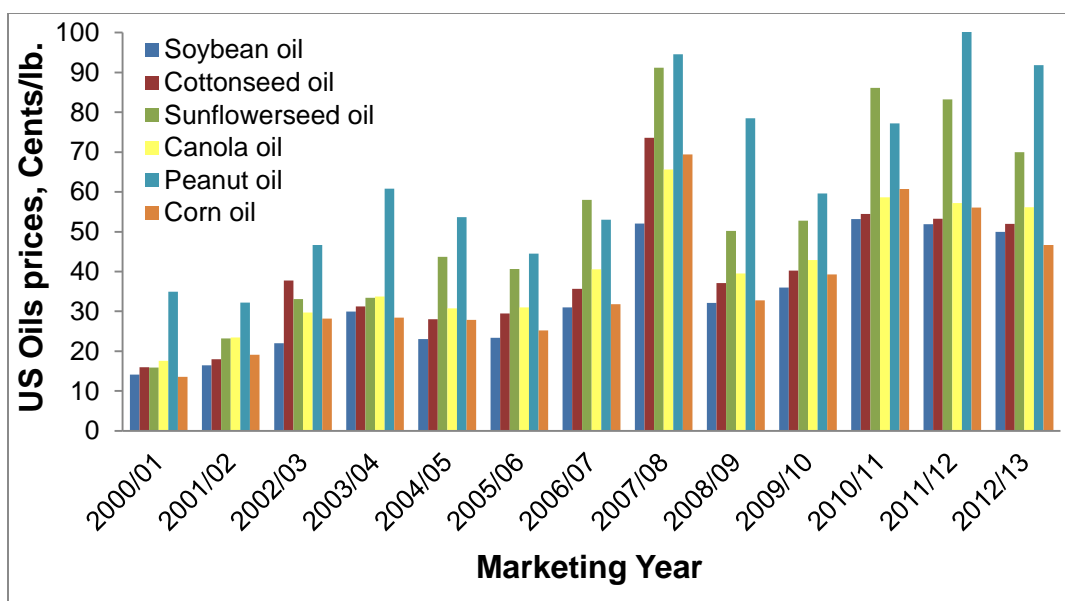


Fig. 2.6: U.S. annual prices for various types of oil from 2000 till 2013 (USDA, 2014a).

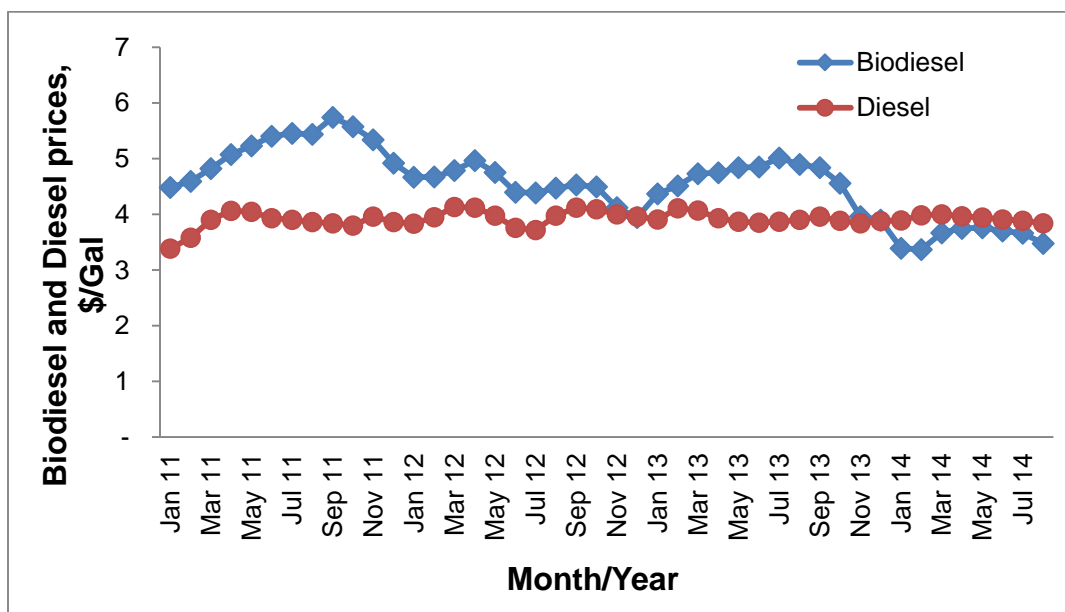


Fig. 2.7: Biodiesel and diesel monthly prices, \$/Gal (USDA, 2014b).

2.2 Biodiesel Production Processes

Around 1899, Rudolf Diesel examined the usage of vegetable oils as fuels for his engine then vegetable oils were utilized as diesel fuels once in a while in the 1930s and 1940s in emergency situations only. But recently, there is a renewed focus on vegetable oils and animal fats to produce biodiesel fuels. Fats and oils are mainly constitute of one mole of glycerol and three moles of fatty acids that are commonly referred to as triglycerides (Ma and Hanna, 1999).

Substituting diesel fuels with vegetable oils/fats, triglycerides, is found to be problematic due to several reasons such as their high viscosity, their low stability against oxidation which subsequently results in polymerization reactions, and their low volatility which increases the ash formation with relatively high amounts because of incomplete combustion. To solve this problem, there were significant efforts to evolve derivatives from vegetable oils/fats that have similar properties and performance of hydrocarbon-based diesel fuels. At least four ways or methods was reported in literature to achieve that such as “Direct use and blending”, “Micro-emulsion”, “Thermal cracking or pyrolysis”, and “Transesterification” (Yusuf et al., 2011).

Among them transesterification (alcoholysis) is considered the most common method of biodiesel production. In which the oil (triglycerides) react with alcohol in the presence of a catalyst to produce fatty acid alkyl esters (biodiesel) and glycerol (by-product). The overall mechanism of transesterification is illustrated in **Fig. 2.8** (Marchetti et al., 2007).

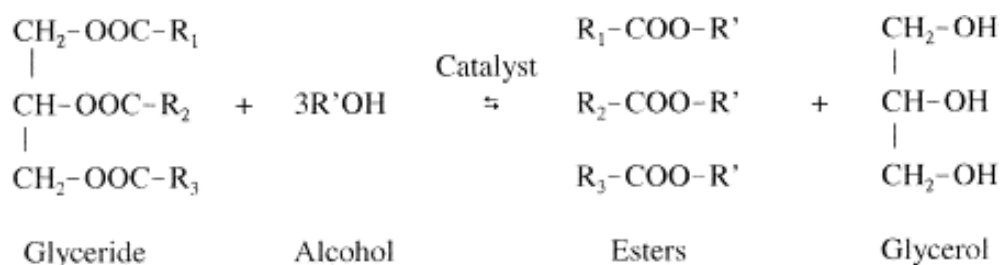


Fig. 2.8: Overall mechanism of transesterification (Marchetti et al., 2007).

Depending on the amount of free fatty acid (FFA) presented in the oil, the suitable catalyst can be selected. Catalysts are basically classified to base, acid, or enzyme. For instance, base-catalyzed reaction gives a better conversion in a relatively short amount of time for triglyceride having lower amount of FFAs, while acid-catalyzed esterification followed by transesterification is more advisable for feedstocks with higher FFAs. Different technologies to produce Biodiesel are used depending on the type of catalyst, reaction temperature needed, amount of free fatty acid in raw materials, and water content of raw materials selected. Homogeneous catalyst method whether involves Base catalyst or Acid catalyst is considered more common than the heterogeneous catalyst one because it is much faster kinetically and is more economically feasible. But its main disadvantage is the high consumption of energy and costly separation of the homogeneous catalyst from the reaction mixture. Enzymatic catalyst such as lipases is used to facilitate the recovery and treatment of the by-product that needs complex processing equipment otherwise but its main downside of enzyme catalyzed process is that the lipases themselves are expensive. Comparison of the different technologies used in biodiesel production can be shown in **Table 2.1** (Helwani et al., 2009)

Table 2.1: Comparison of biodiesel production technologies (Helwani et al., 2009).

Variable	Base catalyst	Acid catalyst	Lipase catalyst	Supercritical alcohol	Heterogeneous catalyst
Reaction temperature (°C)	60–70	55–80	30–40	239–385	180–220
Free fatty acid in raw materials	Saponified products	Esters	Methyl esters	Esters	Not sensitive
Water in raw materials	Interfere with reaction	Interfere with reaction	No influence		Not sensitive
Yields of methyl esters	Normal	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Difficult	Easy		Easy
Purification of methyl esters	Repeated washing	Repeated washing	None		Easy
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium	Potentially cheaper

2.3 Safety and Risk Analysis in Biodiesel Industry

Starting from 2009 many efforts addressed the safety associated with biodiesel production worldwide; probably that's because at that year there was a peak on the number of accidents, around 18 accidents, reported in global biodiesel plants in a time frame of 10 years (Olivares et al., 2014).

First for biofuel generally, there was a study that focused on the analysis of 100 incidents of first generation biofuels that occurred from 2000 to 2009 with an attempt to identify their root factors and find appropriate information on safety issues and lessons learned in the biofuel supply chains. Using statistical methods like multiple correspondence analyses and ascendant hierarchical clustering, an identification of five main incident typologies was conducted in which each typology is illustrated by actual cases of biofuel accidents. From that database, 65% of these accidents were fire and/or explosions occurred in plants, 22% involve transportation accidents with spillage, and 6% include transportation accidents with spillage that resulted in fire and/or explosions. Also, according to main product obtained 33% of the total accidents involve ethanol, 17% include powdered materials, 12% involve biodiesel, and 4% include methanol (Rivière and Marlair, 2010).

Another study was conducted to analyze the fire safety issues in biofuels. In that research, some safety characteristic data (vapor pressure, boiling point, flash point, auto-ignition temperature, and lower explosion limit – upper explosion limit) were addressed to major chemicals involved in bioethanol and biodiesel industries. And some general fire safety considerations were mentioned such as the importance of considering safety data

of the whole list of substances that may be presented on the entire biofuels chains, process safety importance, storage and transport matters, organizational aspects, and end-use problems like occurrence of explosion or fire in refueling stations and vehicles. Also, some incidents related to bioethanol and biodiesel first generation fuels were reviewed (Marlair et al., 2009).

Regarding biodiesel safety specifically, many researchers focused on collecting, reporting and investigating accidents occurred in production plants only while transportation accidents, near misses were beyond their focal point (Salzano et al., 2010b; a; Olivares et al., 2014). Other researchers investigated human error as an important factor in accident happening and related it to the operator's confidence of the biodiesel process simplicity and other causes as errors of commission, omission and neglected actions. As a result of this work a set of recommendations were generated to help minimize it in the biodiesel industry (Rivera and McLeod, 2012).

2.4 Application of Life Cycle Analysis

Life Cycle Assessment (LCA) was proposed in the United States at the Midwest Research Institute around 1970 and shortly it appeared in Europe afterwards. Packaging analysis under environmental aspects, as resource conservation and energy saving, was the main topic then. Also, many other products were analyzed "from cradle to grave" to assess all environmental burdens connected with a product or service starting from raw materials until waste removal stage. It was considered as an environmental assessment tool that involves the balancing of all inputs and outputs inventories (Klöpffer, 1997).

Many studies address Life Cycle Analysis concept from environmental point of view to account for emissions specially Green House Gases (GHG), water foot print, land use, and energy use in biofuels generally and in biodiesel specifically (Kaltschmitt et al., 1997; Kim and Dale, 2005; Larson, 2006; Gnansounou et al., 2009; Yang et al., 2011).

3. PROBLEM STATEMENT AND APPROACH

3.1 Problem Statement

The majority of the studies performed to improve the bio-fuel industry were carried out with focus on economic, environmental or social aspects. Little attention has been given to the safety aspect in the whole analysis. The objective of this work is to include safety into the assessment of the biofuels industry. A life-cycle approach is adopted to include various stages of biomass production and processing. By taking safety into consideration, better understanding of the incident situations may be obtained. Additionally, the work can facilitate more organized and successful emergency response, highlight the areas that need more attention and improvement, and more importantly act towards a life-cycle approach that is aimed at keeping risk within acceptable limits.

3.2 Objective

The basic idea of this research is to conduct a life-cycle assessment of the risks associated with the supply, transportation, processing, storage, production and end use of biomass to bio-fuel in the evolving biodiesel industry sector by assessing technologies and supply chain. This idea is illustrated in **Fig. 3.1**.

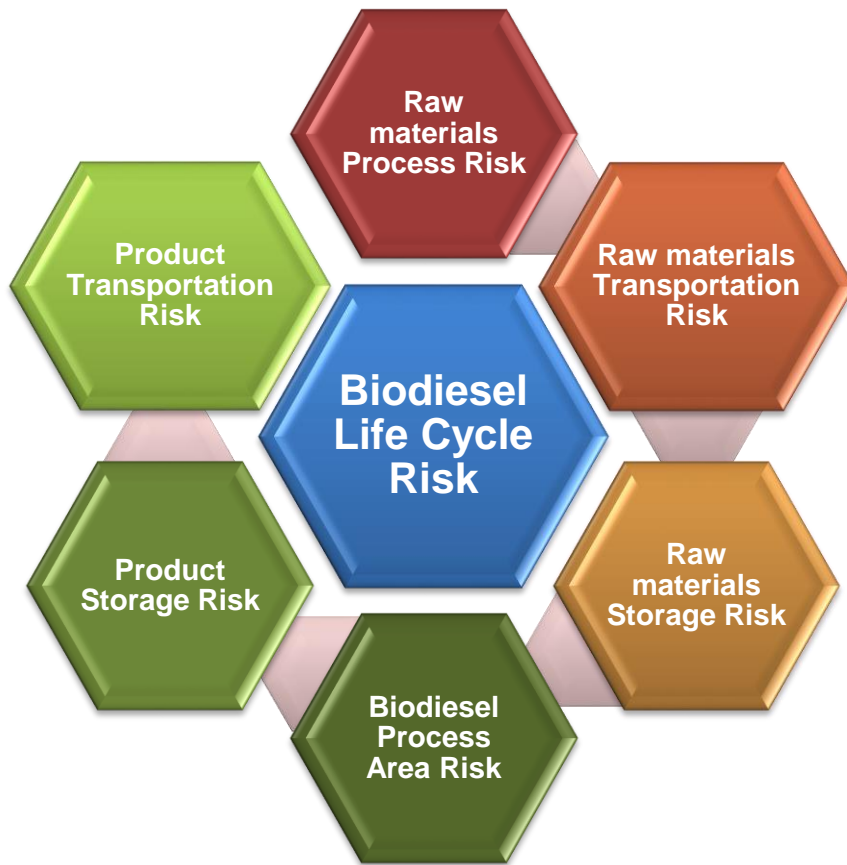


Fig. 3.1 Risk assessment in the whole lifecycle of biodiesel industry.

3.3 Approach

Total Risk calculation for the whole life-cycle will be assessed in a quantitative manner that used afterwards to evaluate the risk trend in the whole biodiesel sector. Quantitative calculation is used to obtain a number that can be a representative to the whole risk per production amount which may be utilized afterwards to anticipate the upcoming loss from the capacity increase.

Then a semi-quantitative risk matrix will be constructed to provide another kind of evaluation to the risk level of the entire industry and subsequently help identifying the rank of each calculated risk level. Risk levels can be acceptable, conditionally acceptable and unacceptable or intolerable. **Fig. 3.2** describes the approach in detail and illustrates all levels of calculations. According to each risk rank resulted, an appropriate action should be considered such as elimination, reduction, mitigation, and or control.

3.4 Methodology

In every stage in the life cycle, the risk will be calculated using the probability of occurrence and the magnitude of consequence or severity in both quantitative and semi-quantitative ways. In order to assess more accurately the risk in the biodiesel whole sector, it is beneficial to study the historical record of the reported accidents/incidents in the last decade. Assessing the risk through databases can help utilizing the real scenarios to know the safety trend involved in the whole biodiesel industry in the recent years.

The data of the biodiesel accidents in the United States were collected from literature (Marlair et al., 2009; Rivière and Marlair, 2010; Salzano et al., 2010a; Olivares et al., 2014), relevant biodiesel magazines, different governmental and official websites (OSHA, EPA, Industrial Fire World) and data bases (Hazmat Intelligence Portal, U.S. Department of Transportation (US DOT, 2014)).

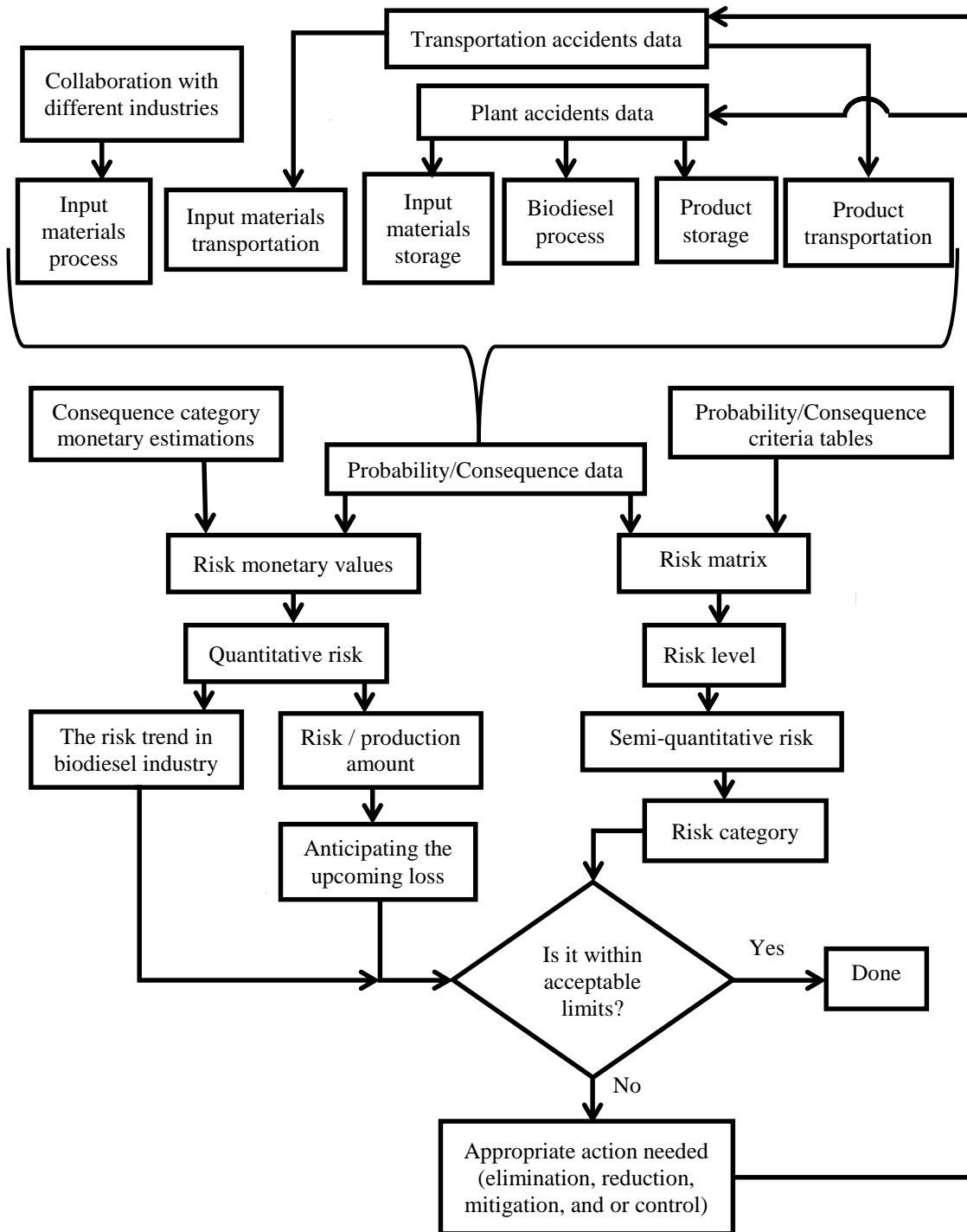


Fig. 3.2: Approach used in the current work to determine the risk profile and the risk matrix in biodiesel industry.

Because these data were reported differently to some extent, the following method was followed to organize the large volume of information. The data were organized first on a yearly basis over the period from 2006 till 2013. And the country of focus will be United States since it has around 68% of all accidents reported in biodiesel plants worldwide (Olivares et al., 2014). Under each year, the following information was searched and completed for plant accidents and/or transportation accidents:

- US and world Biodiesel production
- Number of biodiesel plants in the US (NBB, 2014)
- Number of accidents in each year
- The number and the identity of the states where these accidents occurred
- The type of event when the accident occurred (fire, explosion, spill, etc.)
- The consequence of each accident (fatalities, major and minor injuries, major and minor damages, or not mentioned)
- The location area of the accident occurred in the plant (storage, process, or loading or unloading area)
- The status of the plant in the time of accident (operation, maintenance, or shutdown)
- Mode of transportation (Highway, Rail, Water, etc.) at the time of an accident
- Transportation phase (In transition to storage, Loading, Unloading, etc.) at the time of an accident
- Amount of material transported at the time of an accident

The plant accidents will cover input materials storage, biodiesel process area, and the product (biodiesel and glycerol) storage, whereas transportation accidents will cover input materials transportation, and product (biodiesel) transportation. However, the input materials process risk is beyond the focus of this study because it needs collaboration between different industries depending upon the production method of the selected type of alcohol and/or catalysts.

4. RISK ANALYSIS IN THE U.S. BIODIESEL PLANTS

As mentioned before, biodiesel production is a recently developed industry with a remarkable growth rate. Therefore, an insight in the risk analysis of such industry is necessary to highlight the areas that need more attention and improvement. In order to assess more accurately the risk in the biodiesel whole sector, it is beneficial to study the historical record of the reported accidents/incidents in the last decade. Assessing the risk through databases can help utilizing the real scenarios to know the safety trend involved in the whole biodiesel industry in the recent years.

In this section, an assessment for the risk associated with the biodiesel production was first made using data collected for the biodiesel incidents/accidents occurred in the United States over the period from 2006 till 2013. The data were then used to calculate the risk level as a function of time and the corresponding risk matrix was constructed afterwards.

4.1 Data Analysis

The data of the biodiesel plant accidents in the United States are summarized in the Appendix as **Tables A-1, A-2, and A-3**. Also, as previously shown in **Fig. 1.1**, the world and US biodiesel production over the period between 2006 and 2013 have been increasing with 230% (3 folds) and 260% (7 folds) for world and US, respectively.

The drop in the biodiesel production in 2010 can be explained by looking at the number of plants in each year. As depicted in Table A-1, this number dropped significantly

from 173 in 2009 to 100 in 2010 and then increased again, with fluctuation, till 155 in 2013. This fluctuation was considered when the risk analysis was performed.

Fig. 4.1 shows the distribution of the number of accidents in this period of eight years. The figure shows an increase in the number of accidents till 2009, which represents a peak with 14 accidents, and then a fluctuation till 2013 which has highest value, 8 accidents, after that time.

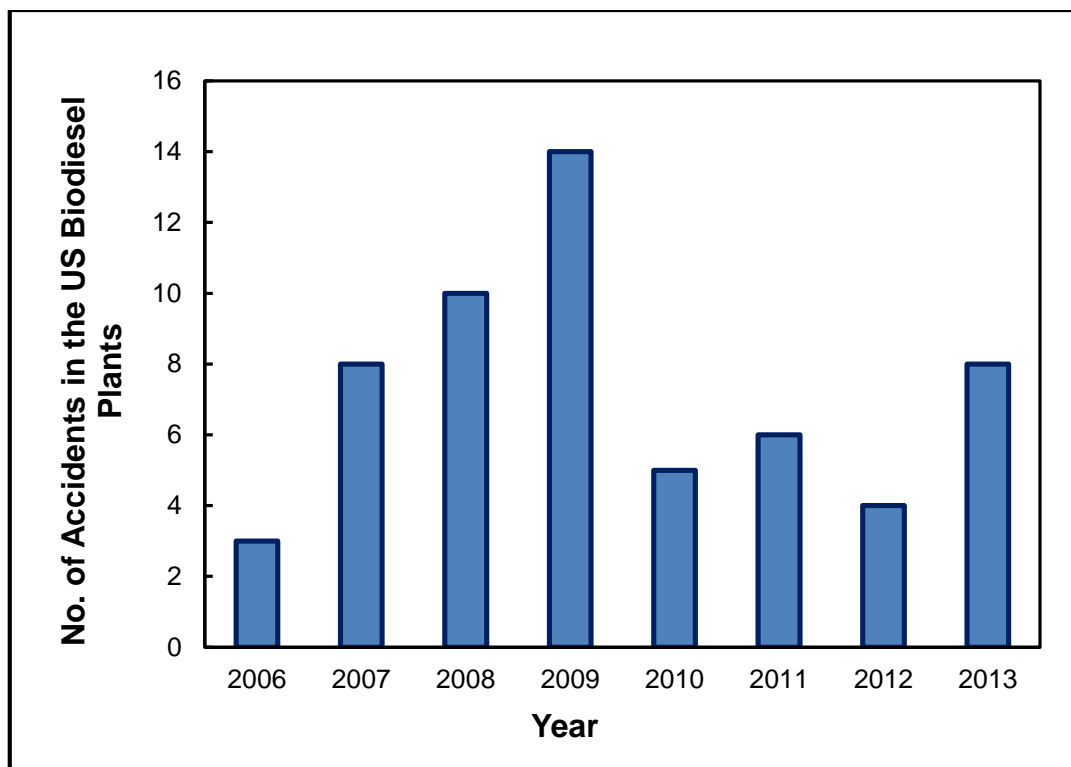


Fig. 4.1: Number of accidents in the U.S. biodiesel plants from 2006 till 2013.

Then the data was also normalized by the number of plants in each year and the result is shown in **Fig. 4.2**. In this form, the data represents the frequency of accidents in each year and shall be used for further risk calculations.

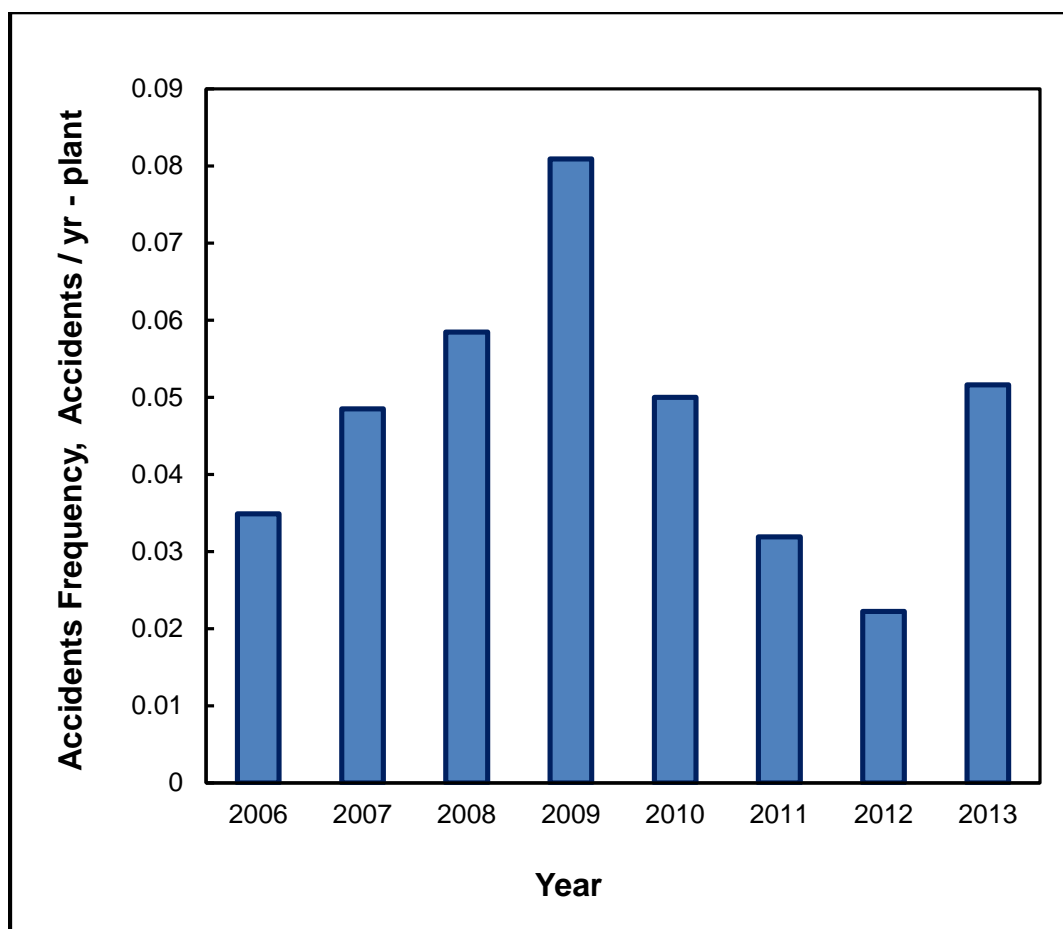


Fig. 4.2: Normalized number of accidents in the U.S. biodiesel plants from 2006 till 2013.

For an industry that started commercially in the late nineties (Atabani et al., 2012), the trend for incidents/accidents frequency was increasing till 2009 followed by a steady decrease till 2102. However in 2013, the frequency of accidents increased again and is slightly higher than of 2010. At the first glance, one can conclude from the safety point of view that production hazards have probably increased recently which is sometimes misleading because incidents/accidents outcomes may be way less. So it worth noting that; it is very important to assess in terms of the risk not just the frequency. Moreover, a continuous monitoring of these types of data along with following/applying the safety measurements and regulations are necessary for such a growing industry.

An analysis of the accidents consequences is shown below. Among the different types of consequences, a damage (whether is major or minor) is always associated with an accident as shown in **Fig. 4.3**. No fatalities were reported in accidents from 2009 till 2011 and beside a single accident in 2009 which involved 19 minor injuries; no accident involved more than 4 minor injuries. Major injuries were vanishing after 2010 as depicted in **Fig. 4.4**.

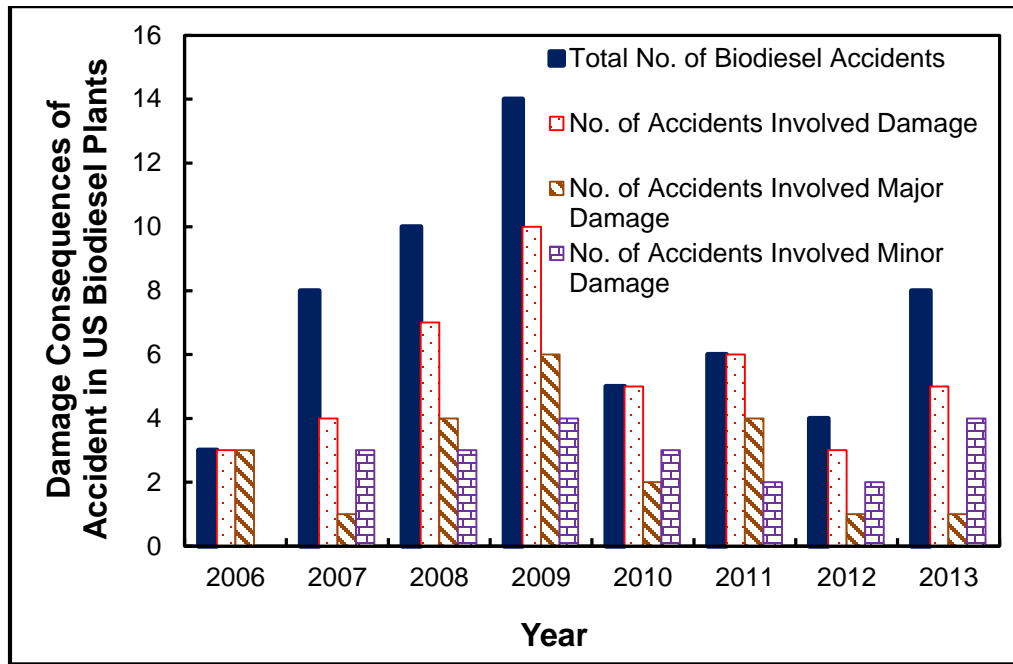


Fig. 4.3: Damage consequences in the U.S. biodiesel plants from 2006 till 2013.

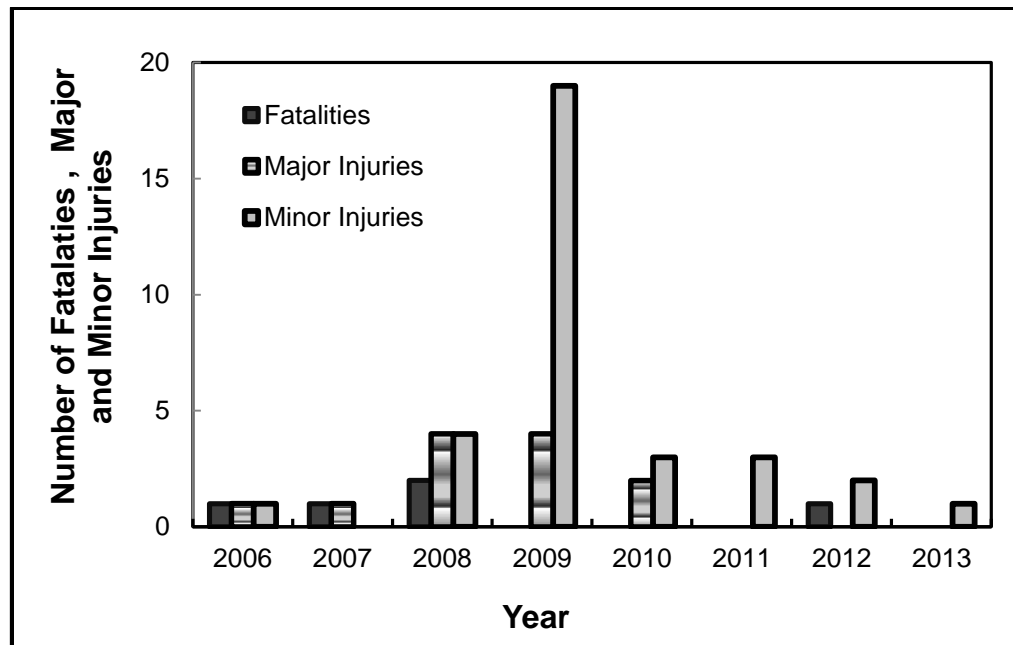


Fig. 4.4: Number of fatalities and injuries in the U.S. biodiesel plants from 2006 till 2013.

It can be concluded for biodiesel accidents that, a fire (whether accompanied with spill or explosion or alone), is more likely to occur as shown in **Fig. 4.5**.

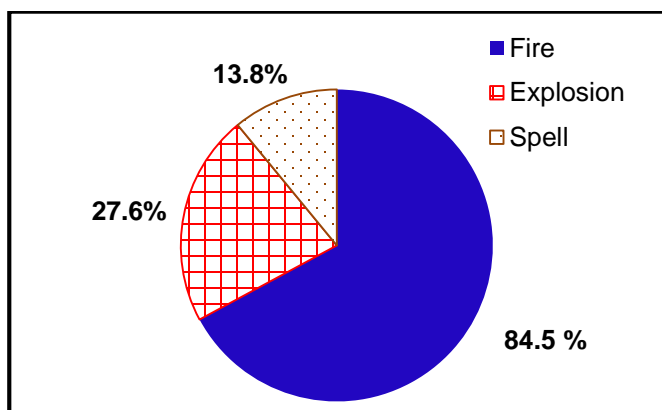


Fig. 4.5: Type of the accident event for the U.S. biodiesel plants from 2006 till 2013.

Revising the data showed that there is an overlap of the percentage of each type category shown in **Fig. 4.5**. Therefore, these percentages are sum up to more than 100% of the total number of accidents; as one single accident might have a fire, an explosion, and/or a spillage happened at the same time. The second possibility is an explosion which in most cases is a trigger for a fire as can be seen from **Table 4.1**. The highest calculated probability is for Fire only type followed by Fire and Explosion one. Moreover, Spill only or Explosion only types are much less probable to happen because usually they will result in a fire due to the non-confinement of flammable chemicals involved in the process.

Table 4.1: Number and probability of event type in the U.S. biodiesel accidents.

Accident	Fire only	Fire, Spill	Fire, Explosion	Spill only	Spill, Explosion	Explosion only
Number	29	8	12	4	1	3
Probability	0.5	0.1379	0.2069	0.069	0.0172	0.0517

Most of the incidents/accidents were reported to occur in the process area, with a percentage of 43% of the total number, followed by the storage area, with a percentage of 33%, as shown in **Fig. 4.6**. This is expected because these two areas contain all active and hazardous materials with much higher probability of finding sources of ignitions and/or fires. One fifth of the accidents investigated were found to be with limited or undetermined information regarding the specific location of the incidents and/or accidents studied.

It worth mentioning that, 75% of these No information type of accidents were recognized over the 3 year period between 2007 and 2009; that's may be due to the limited awareness of the importance of complete and accurate reporting and/or the insufficient realization of the principle hazards associated with the production.

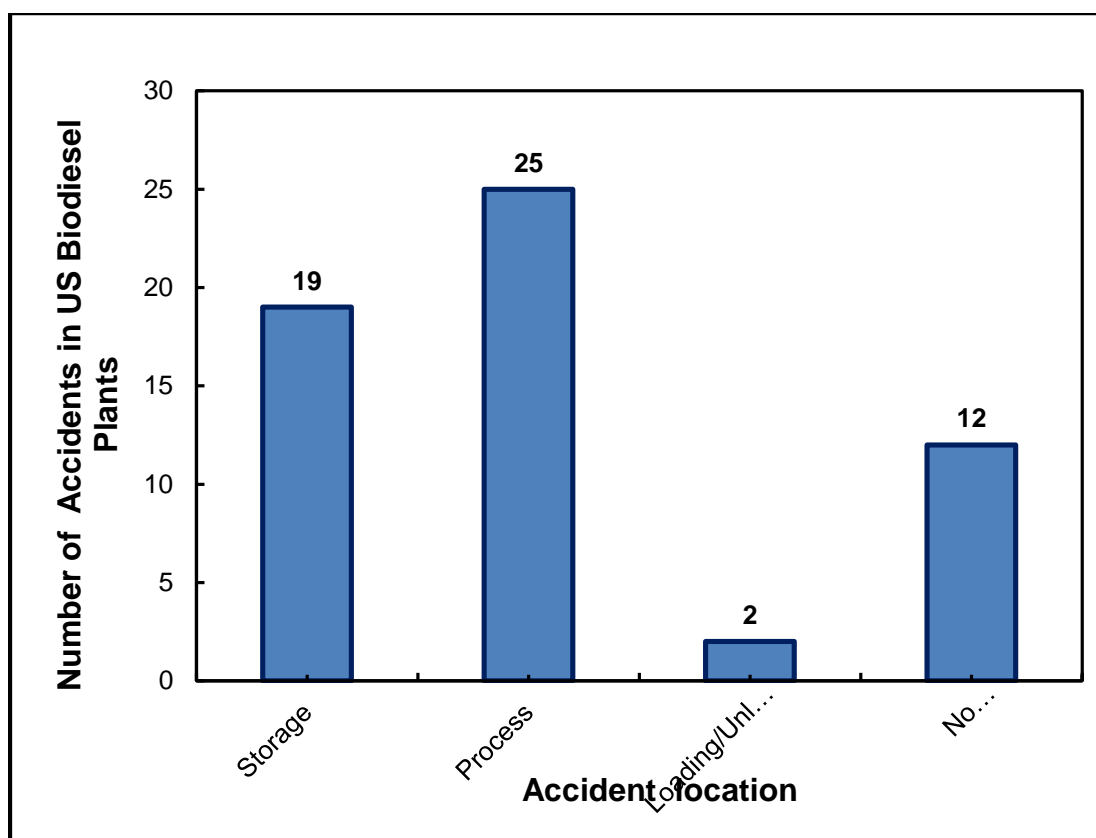


Fig. 4.6: Locations of accident in the U.S. biodiesel plants from 2006 till 2013.

Investigation of the 19 accidents occurred in the storage areas whether involved input chemicals, product or byproduct revealed that methanol (a main reactant) comes after the final product (biodiesel) as the main chemicals leading to incidents/accidents in the US biodiesel facilities as shown in **Fig. 4.7**. This is mainly because methanol is highly flammable, explosive and toxic chemical that has a nearly invisible flame when burns while biodiesel is considered a flammable-combustible liquid that most of the times still have some methanol residues in it. Sulfuric acid contributed to around 21% of the storage accidents and biomass, vegetable oil, only resulted in one accident.

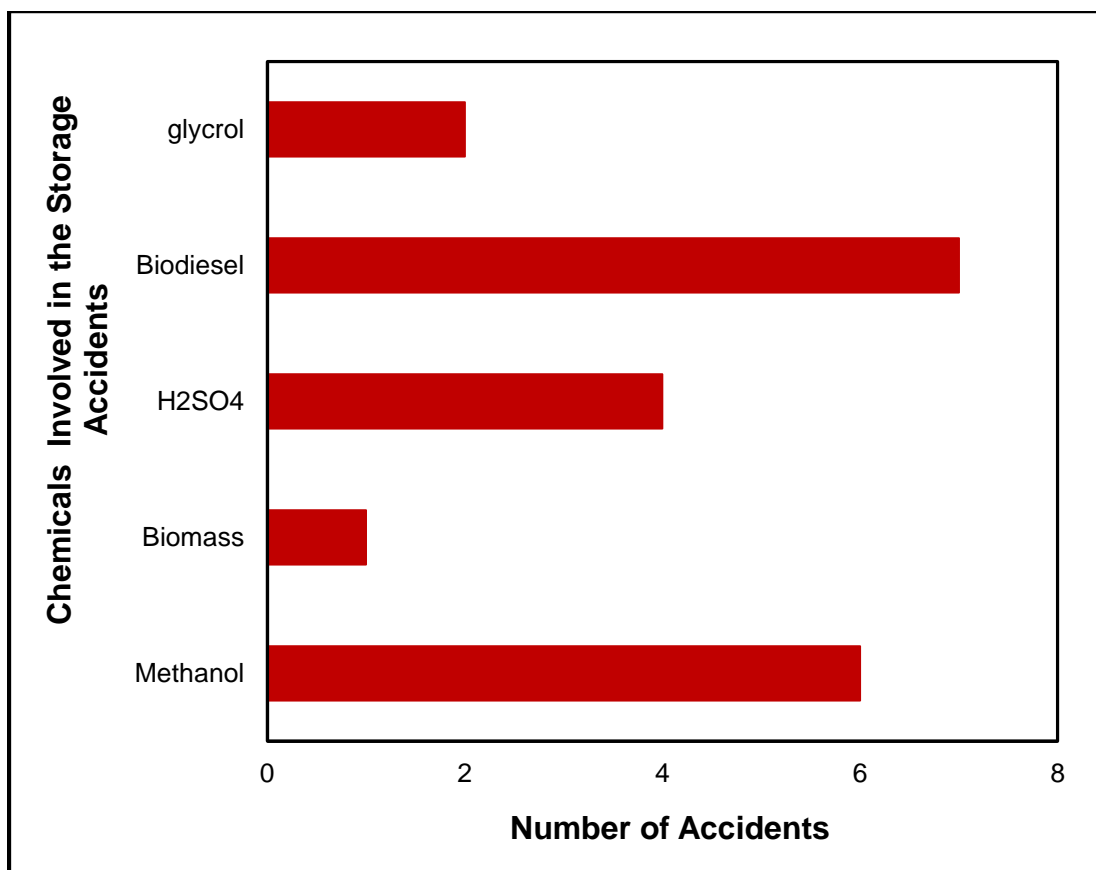


Fig. 4.7: Chemicals involved in storage accidents of the U.S. biodiesel plants over the period between 2006 and 2013.

Fig. 4.8 illustrates the status of the process when an accident occurs, and the data show that 64% of the accidents occurred while the plant was in operation followed by a 21% of undetermined status while 10% when the plant was shut down. This is anticipated because most of the time the plant is in operational status and more vulnerable to mechanical failure or malfunctions that may lead to leakage, heat increase, pressure build up, and spontaneous combustion.

In addition, the data show that operator error happened many times during operation, especially through the neutralization step where an overpressure resulted from improper mixing of more than needed sulfuric acid to the glycerol which leads to exothermic reaction, and finally tank explosion.

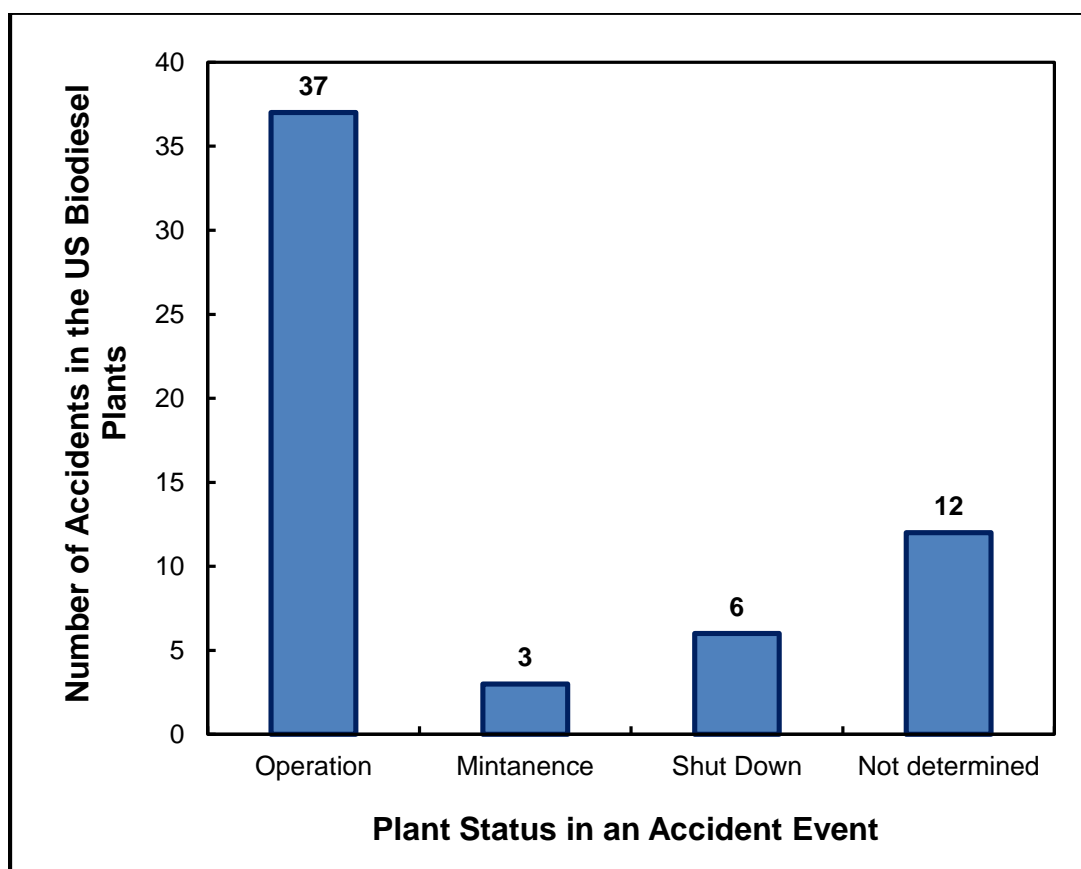


Fig. 4.8: Plant status in an accident event for the U.S. biodiesel plants from 2006 till 2013.

4.2 Risk Calculations

The data reported for these accidents were used to calculate the total risk for each year using a quantitative technique that was used afterwards to evaluate the risk trend in the whole biodiesel sector in the United States over the period between 2006 and 2013. Then, a simple, quick and easy-to-build semi-quantitatively risk matrix was constructed. This matrix provides another kind of evaluation of the risk level of the entire industry on a yearly basis and subsequently helps identify the rank of each calculated risk level such as acceptable, conditionally acceptable and unacceptable or intolerable.

According to each risk rank, an appropriate action should be considered whether elimination, reduction, mitigation, and or control. It is also important to mention that there may be other incidents/accidents that have also occurred without reporting or external communication through the media. Moreover, taking near misses into account will definitely help to obtain more accurate risk assessment.

4.2.1 Quantitative Risk Calculations

The technique which was followed through these calculations is outlined below:

- 1- Probability of each category of consequence (fatality, major injury, minor injury, major damage and minor damage) is calculated with different units as a function of time (year) over the period under investigation (from 2006 to 2013) as follows:

$$P(\text{Consequence})/\text{Accident} \cdot \text{year} = \left(\frac{\text{Number of consequence}}{\text{Number of accidents}} \right)_{\text{year}} \quad (4.1)$$

$$P(\text{Consequence})/\text{Plant} \cdot \text{year} = P(\text{Consequence}/\text{Accident}) * P(\text{Accidents})/\text{Plant} \cdot \text{year} \quad (4.2)$$

$$P(\text{Consequence/Accident}) = \left(\frac{\text{Number of consequence per year}}{\text{Number of accidents}} \right) \quad (4.3)$$

$$P(\text{Accidents})/\text{Plant} \cdot \text{year} = \left(\frac{\text{Number of accidents}}{\text{Number of plants}} \right)_{\text{year}} \quad (4.4)$$

$$P(\text{Consequence})/\text{Biodiesel production} \cdot \text{year} = \left(\frac{\text{Number of consequence}}{\text{amount of biodiesel produced}} \right)_{\text{year}} \quad (4.5)$$

2- The magnitude of each consequence category was estimated based on data published in literature (Corso et al., 2006; NSC, 2013; Kip Viscusi, 2014) and these estimate values are listed in **Table 4.2**. Also it worth mentioning that, these kinds of estimations are on an average basis and are just used to facilitate expressing the risk for each consequence category in terms of monetary value and to ease further necessary computations to obtain the total risk as a cumulative one number.

Table 4.2: Monetary estimation of the magnitude of each consequence category.

Type of Consequence	Magnitude, \$M
Fatality	7
Major Injury	3
Minor Injury	0.05
Major Damage	5
Minor Damage	0.5

3- The risk of each category of consequence was calculated by multiplying the Probability of the consequence (fatalities, injuries, damage) by the magnitude of each category of consequence. Three types of risk were calculated per each category of consequence and that according to the selected type of normalization used for the probability values, whether by the number of accidents, plants, or the production volume of biodiesel as illustrated in the next equations:

$$\begin{aligned} \text{Risk of consequence/Accident . year} \\ = P(\text{Consequence})/ \text{Accident . year} \times \text{Magnitude of consequence} \end{aligned} \quad (4.6)$$

$$\begin{aligned} \text{Risk of consequence/Plant . year} \\ = P(\text{Consequence})/ \text{Plant . year} \times \text{Magnitude of consequence} \end{aligned} \quad (4.7)$$

$$\begin{aligned} \text{Risk of consequence/Biodiesel production . year} \\ = P(\text{Consequence})/ \text{Biodiesel production . year} \times \text{Magnitude of consequence} \end{aligned} \quad (4.8)$$

The total risk in each year is simply calculated as the summation of risk of each category of consequence in this year.

$$\begin{aligned} \text{Total risk in specific year} = & \text{Risk of fatality} + \text{Risk of major injury} + \text{Risk of minor injury} + \\ & \text{Risk of major damage} + \text{risk of minor damage} \end{aligned} \quad (4.9)$$

A summary of the calculated risk for each category of consequence per year following equations (4.1) to (4.9) is shown in **Table 4.3**, **Table 4.4**, and **Table 4.5**.

Table 4.3: A summary of the total risk per accident per year calculations.

Year	R(F), \$	R(MI), \$	R(mI), \$	R(MD), \$	R(mD), \$	RT, \$
2006	2,333,350	1,000,000	16,670	5,000,000	0	8,350,000
2007	875,000	375,000	0	625,000	187,500	2,062,500
2008	1,400,000	1,200,000	20,000	2,000,000	150,000	4,770,000
2009	0	857,150	67,860	2,142,860	142,860	3,210,720
2010	0	1,200,000	30,000	2,000,000	300,000	3,530,000
2011	0	0	25,000	3,333,350	166,670	3,525,000
2012	1,750,000	0	25,000	1,250,000	250,000	3,275,000
2013	0	0	6,250	625,000	250,000	881,250

Table 4.4: A summary of the total risk per plant per year calculations.

Year	R(F), \$	R(MI), \$	R(mI), \$	R(MD), \$	R(mD), \$	RT, \$
2006	81,400	34,890	585	174,420	0	291,280
2007	42,425	18,180	0	30,300	9,090	100,000
2008	81,870	70,175	1,170	116,960	8,770	278,950
2009	0	69,365	5,495	173,410	11,560	259,830
2010	0	60,000	1,500	100,000	15,000	176,500
2011	0	0	800	106,385	5,320	112,500
2012	38,890	0	560	27,780	5,560	72,780
2013	0	0	325	32,260	12,900	45,480

Expressing the risk of each consequence category and the total risk in different forms like shown above provides some insights about the safety of biodiesel from various perspectives and provide a useful evaluation to the safety trend.

Table 4.5: A summary of the total risk per production per year calculations.

Year	R(F), \$	R(MI), \$	R(mI), \$	R(MD), \$	R(mD), \$	RT, \$
2006	28,000	12,000	200	60,000	0	100,000
2007	14,300	6,100	0	10,200	3,060	36,690
2008	20,650	17,700	300	29,500	2,210	70,340
2009	0	23,300	1,840	58,160	3,900	87,150
2010	0	17,500	440	29,120	4,400	51,400
2011	0	0	160	20,700	1,040	21,860
2012	7,100	0	100	5,050	1,000	13,220
2013	0	0	40	3,700	1,500	5,190

Where:

R(F) = risk due to fatalities in this year

R(MI) = risk due to major injuries in this year

R(mI) = risk due to minor injuries in this year

R(MD)= risk due to major damages in this year

R(mD)= risk due to minor damages in this year

R(T) = total risk in a specific year over the period 2006-2013

Figs. 4.9 to 4.11 indicates that year of 2006 had the peak value for total risk while year 2013 has the lowest value. The data show a decrease in the risk with time from 2006 till 2007. Afterwards, with the exception of 2010 in **Fig. 4.9**, the risk showed a decreasing profile until 2013 with values that are significantly lower than those in 2007. The increase in the risk in 2006 is due to the lowest value of the denominator in the probability expressions; whether the number of accidents occurred, the number of biodiesel plants,

and the level of biodiesel production. These representations also indicate an improvement in the implementation of safety regulation and precautions in the US biodiesel industry.

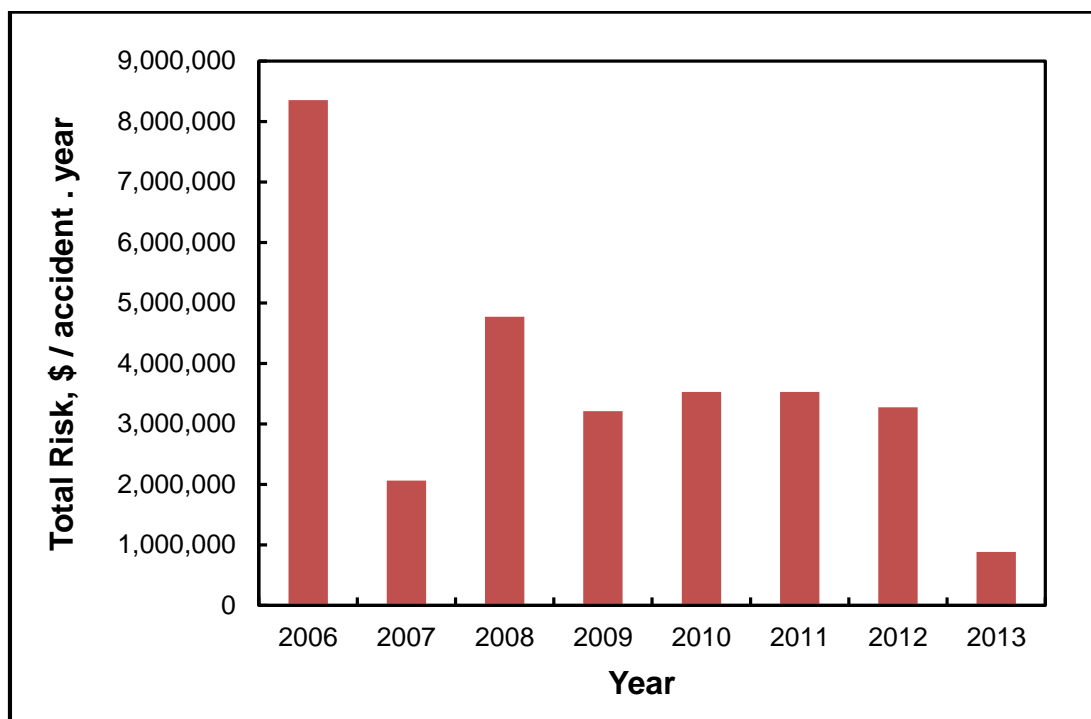


Fig. 4.9: Total Risk per accident per year in the U.S. biodiesel plants from 2006 till 2013.

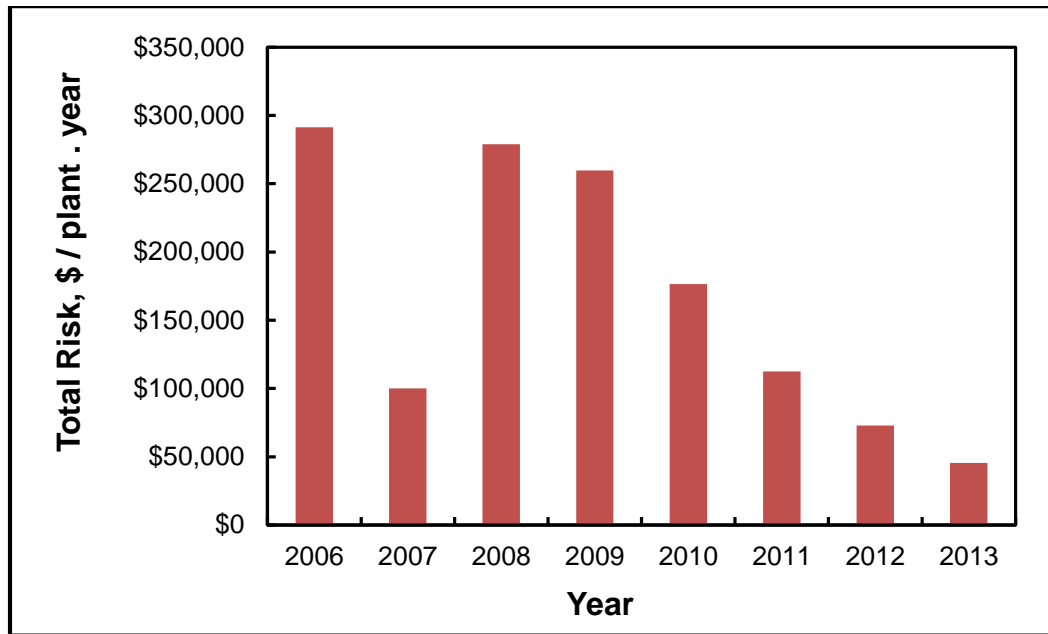


Fig. 4.10: Total Risk per plant per year in the U.S. biodiesel plants from 2006 till 2013.

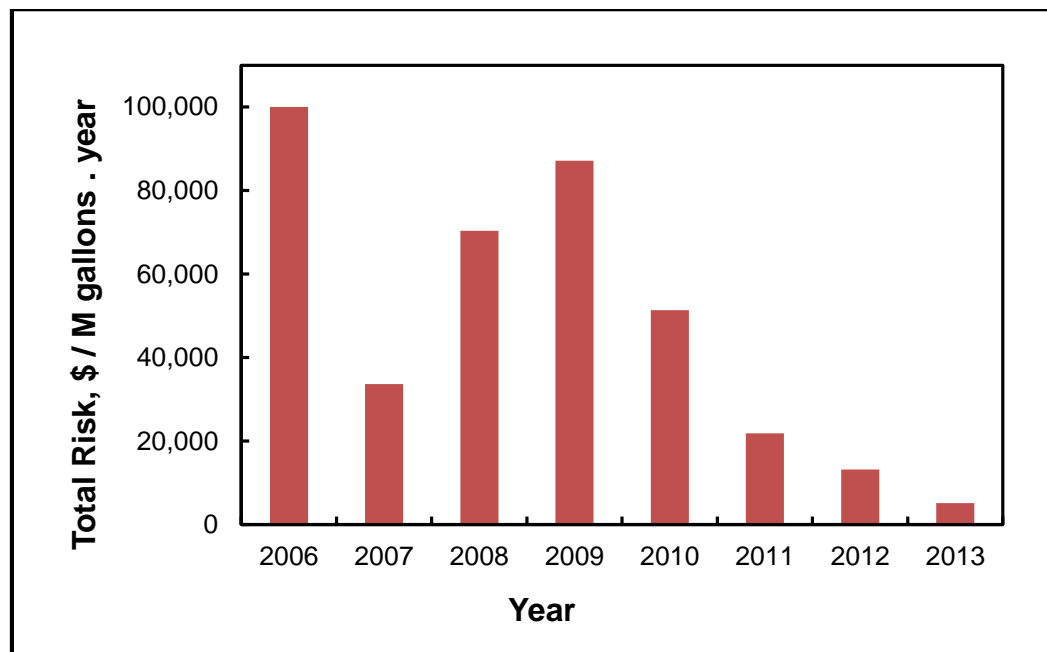


Fig. 4.11: Total Risk per amount of production per year in the U.S. biodiesel plants from 2006 till 2013.

4.2.2 Semi-quantitative Risk Matrix

A risk matrix is usually utilized to perform rank ordering to the potential risk in two dimensions with frequency or probability of occurrence along Y axis and consequence magnitudes or severities along X axis. These two axes are defined according to either qualitative or semi-quantitative criteria, stated in the probability and consequence tables, and the two axes intersection generated the matrix cells that illustrate risk level (Ericson, 2011).

It should be noted that; the risk matrix can be tailored for any project to meet its specific needs. Also, the semi-quantitative criterion is preferred over the qualitative one to help decrease ambiguity, subjectivity and bias (Smith et al., 2009); which in turn leads to more clear and accurate representation to the potential risk and consequently making more informative decisions.

In the current study, the definition of the probability scale, the severity or the consequence scale, and Risk Assessment Matrix were adopted and modified from what was reported in MIL-STD-882E (US Department of Defense, 2012) as shown in **Table 4.6**, **Table 4.7** and **Table 4.8**. While **Table 4.9** addresses some of the information needed for performing further risk management. Risk Categories and Actions needed in **Table 4.9** were adopted and modified from what was reported in literature (Markowski and Mannan, 2008).

Table 4.6: Probability levels, (modified from the U.S. Department of Defense, 2012).

Description	Level	Quantitative description
Frequent	A	Probability of occurrence $\geq 10^{-1}$
Probable	B	$10^{-2} \leq$ Probability of occurrence $< 10^{-1}$
Occasional	C	$10^{-3} \leq$ Probability of occurrence $< 10^{-2}$
Remote	D	$10^{-6} \leq$ Probability of occurrence $< 10^{-3}$
Improbable	E	Probability of occurrence $< 10^{-6}$
Eliminated	F	Incapable of occurrence within the life of an item, or no information is available

Table 4.7: Severity categories, (modified from the U.S. Department of Defense, 2012).

Description	Category	Mishap Result Criteria
Catastrophic	1	Could result in one significant or more of the following: death, permanent disability, irreversible significant environmental impact, or monetary loss equal to or exceeding \$10M.
Critical	2	Could result in one significant or more of the following: permanent partial disability, injuries or occupational illness that may result in hospitalization of at least three personnel, reversible significant environmental impact, or monetary loss equal to or exceeding \$1M but less than \$10M.
Marginal	3	Could result in one significant or more of the following: injuries or occupational illness that may result in one or more lost work day(s), reversible moderate environmental impact, or monetary loss equal to or exceeding \$100K but less than \$1M.
Negligible	4	Could result in one significant or more of the following: injuries or occupational illness that does not result in one or more lost work day(s), minimal environmental impact, or monetary loss less than \$100K.
None	5	Did not result in any significant consequences, or no information is available

Table 4.8: Risk assessment matrix, (modified from the U.S. Department of Defense, 2012).

Severity Probability	Catastrophic (1)	Critical (2)	Marginal (3)	Negligible (4)	None (5)
Frequent (A)	High	High	Serious	Medium	Eliminated
Probable (B)	High	High	Serious	Medium	
Occasional(C)	High	Serious	Medium	Low	
Remote(D)	Serious	Medium	Medium	Low	
Improbable(E)	Medium	Medium	Medium	Low	
Eliminated (F)	Eliminated				

Table 4.9: Risk levels, risk categories, and actions needed.

Risk Levels	Risk Categories	Actions needed
High	Non-Acceptable	Must change immediately
Serious	Tolerable-Unacceptable	Additional safety measures are required in medium notice
Medium	Tolerable-Acceptable	Further action is based on ALARP principle
Low	Acceptable	No further action is required
Eliminated	Undetermined	More information needed for a decision

Where ALARP states for ‘As Low As Reasonably Practicable’ which means that the risk level indicated should be reduced without extremely expensive safety improvements that reached after certain point of further risk-reduction (Jones-Lee and Aven, 2011).

The following approach was followed in order to build the risk matrix:

- 1- Each accident was treated separately and independently
- 2- The probability of each accident was calculated by dividing the number of accidents in each year by the number of working plants in this year as follows:

$$P(\text{accident})_{\text{year}} = \left(\frac{\text{Number of accidents}}{\text{Number of plants}} \right)_{\text{year}} \quad (4.10)$$

- 3- According to the type of the consequences in each accident, the level of severity was determined following the guidelines in **Table 4.2**.
- 4- According to the probability and the level of severity, each accident was allocated in a cell in the safety matrix and the total number of accidents in each cell was determined.

Table A-4 summarizes the severity level, probability level, and risk level of each accident. It was observed that all accidents fell in the category of the “probable” events, however with different severities which ranged from “None” to “Catastrophic”. The “None” in this work refers to an accident which did not result in any significant consequence or no information was reported related to this accident.

According to this analysis, **Table 4.10** shows the biodiesel risk matrix representation between 2006 and 2013. Over this time period, 10% of the biodiesel accidents were catastrophic, 15% were critical, and 40% resulted in negligible consequences. Whereas in terms of risk, 36% of the accidents are not acceptable and need immediate change, 14% require in medium notice additional safety measures while 40% need further action based on ALARP principle.

Table 4.10: Biodiesel risk matrix representation between 2006 and 2013.

Severity Probability	Catastrophic (1)	Critical (2)	Marginal (3)	Negligible (4)	None (5)
Frequent (A)	High	High	Serious	Medium	Eliminated
Probable (B)	6 (10%)	15 (26%)	8 (14%)	23 (40%)	
Occasional(C)	High	Serious	Medium	Low	
Remote(D)	Serious	Medium	Medium	Low	
Improbable(E)	Medium	Medium	Medium	Low	
Eliminated (F)	Eliminated				

Where,

6 (10%) for example means 6 accidents or 10% of the total accidents over the whole period from 2006 to 2013.

It is also important to examine the safety matrix and the risk level of the biodiesel industry in the specified period from time perspective to help display its trend over time. So in this study, a dynamic mapping to Risk Assessment Matrix is presented, in which the risk level is determined as a function of time (year) over the period of the selected eight years from 2006 to 2013. **Table 4.11** shows the cumulative data over the whole investigated period, where, each cell in the matrix represent how many accidents occurred in every year with the risk level resulted.

Table 4.11: Dynamic mapping to risk assessment matrix for the biodiesel industry in the U.S. over the period between 2006 and 2013.

Severity Year	Catastro- phic	Critical	Marginal	Negligible	None	Total accidents number
2006	1, High	2, High	0	0	0	3
2007	1, High	0	1, Serious	3, Medium	3, Eliminated	8
2008	3, High	1, High	1, Serious	2, Medium	3, Eliminated	10
2009	0	7, High	2, Serious	3, Medium	2, Eliminated	14
2010	0	2, High	1, Serious	2, Medium	0	5
2011	0	0	3, Serious	3, Medium	0	6
2012	1, High	0	0	3, Medium	0	4
2013	0	1, High	0	6, Medium	1, Eliminated	8

5. RISK ANALYSIS IN THE U.S. BIODIESEL TRANSPORTATION

As stated earlier, biodiesel production has been growing significantly in recent decades. Conducting a risk analysis in each sector of such a developing industry is necessary to determine the areas which need more attention and improvement. Therefore, while section four was concerned with the risk in the biodiesel plants; this section addresses the accidents and the associated risk in the transportation sector. The record of the reported accidents/incidents (US DOT, 2014) over the period between 2006 and 2013 was investigated and analyzed using the same technique followed in the previous section. The output from this analysis is the quantitative risk with two different units (\$/accident and \$/amount transported) for every selected input chemical and product. The analysis will also address the risk level associated with the transportation of input chemicals and product and the corresponding risk matrix as a function of time.

5.1 Life Cycle Assessment in the Risk Analysis

Production of biodiesel is attainable via several processes as discussed in details previously. Throughout each of these processes, various chemicals can be used as raw materials, catalysts, or neutralizing agents. Instead of limiting the risk analysis on the final product only (biodiesel), the concept of the life cycle has the advantage of involving all these chemicals in the risk determination process to account for the risk carried by these chemicals to the production step. In such approach, the contribution of each of these

chemicals is calculated, normalized, and added to determine the total risk in the biodiesel transportation.

This approach, however, faces two challenges. First, biodiesel production routes are numerous and thus various types of chemicals are involved as well. Secondly, available data were very limited on the transportation of biodiesel itself, which is probably due to the young age of such industry. Therefore, developing a holistic risk assessment based on the concept of life cycle is in fact very important, because this assessment can be updated periodically once the data on the biodiesel accidents are recorded.

The first challenge was resolved by focusing on a dominant biodiesel process (alkali-catalyzed transesterification) and selecting the involving reactant (methanol), catalyst (sodium hydroxide and sulfuric acid, for alkaline based process and acidic pretreatment or esterification, respectively). Also, sulfuric acid was used as a neutralizing agent. However, the second challenge was resolved by selecting diesel fuel as a good representative for biodiesel. Diesel fuel would have similar performance properties to biodiesel and is expected to result in similar consequences if the latter is involved in an accident.

5.2 Data Analysis

Data were mainly collected from the Hazmat Intelligence Portal, U.S. Department of Transportation website (<http://www.phmsa.dot.gov/hazmat>). Data on the number of accidents, phase and mode of transportation, the type of events, and the causes of failure of the accidents for each chemical will be first discussed. The consequences of these incidents including the number of fatalities, injuries, and damage for the transportation of the input chemicals (methanol, sodium hydroxide, and sulfuric acid) plus the diesel fuel (as replacement for the biodiesel) will then be used to determine the risk in both quantitative and semi- quantitative manners.

The total risk was normalized by the amount transported of each chemical and then converted to a basis of biodiesel produced using an overall mass target method. This last step is necessary to assure that the portion of risk which these chemical are introducing to the biodiesel transportation is only used, and not the total risk associated with the transportation of these chemical in the U.S. over the investigated period.

5.2.1 Input Chemicals

The number of accidents resulted from the transportation of each of the input chemicals is shown in **Fig. 5.1**. The data reveals that methanol and sulfuric acid were associated with larger number of accidents than sodium hydroxide in solid state (as it is used in the biodiesel process). A reduction in the number of accidents for the sulfuric acid is remarkably observed from 2006 till 2011 with almost 48% (from 305 to 159 accidents) followed by a slight increase till 2013(177 accidents). The number of accidents in

methanol transportation was fluctuating between 210 and 300 with an average of 250 accidents per year, while sodium hydroxide transportation resulted in an average of 50 accidents per year.

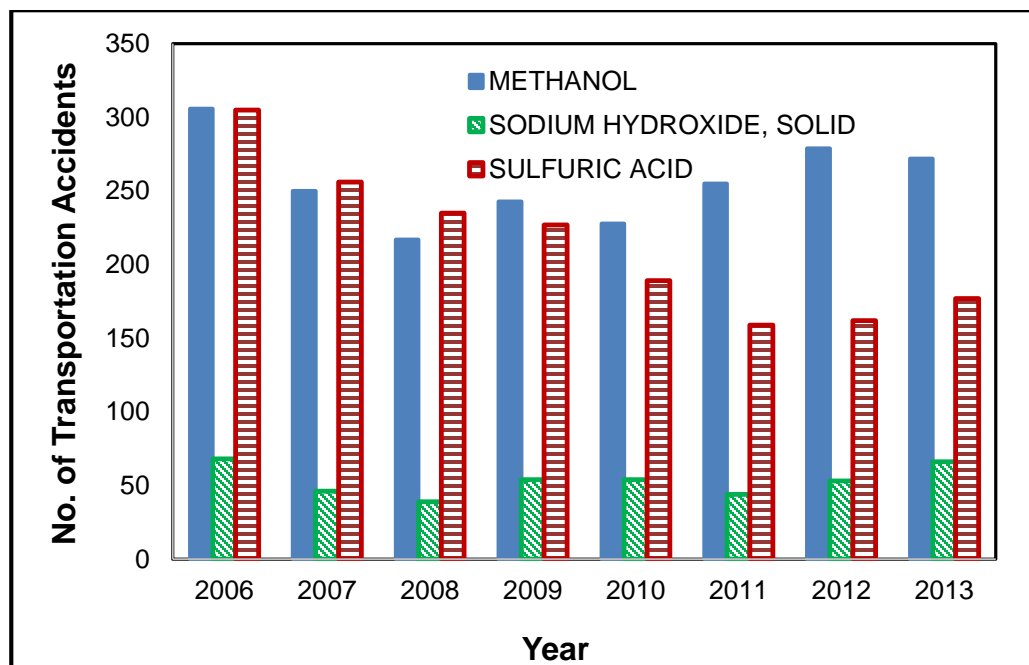


Fig. 5.1: Number of accidents associated with the transportation of each of the selected input chemicals to the biodiesel production over the period between 2006 and 2013.

Each of these chemical was transported in different mode of transportation including trucks on highway roads, railways, water, and air. **Fig. 5.2** demonstrates that the highway transportation mode is the dominant transportation mode involves accidents while a slight contribution of the railways is observed especially in the transportation of sulfuric acid. Revising the number of accidents discussed above suggests that railways might be safer mode of transportation than on highway roads.

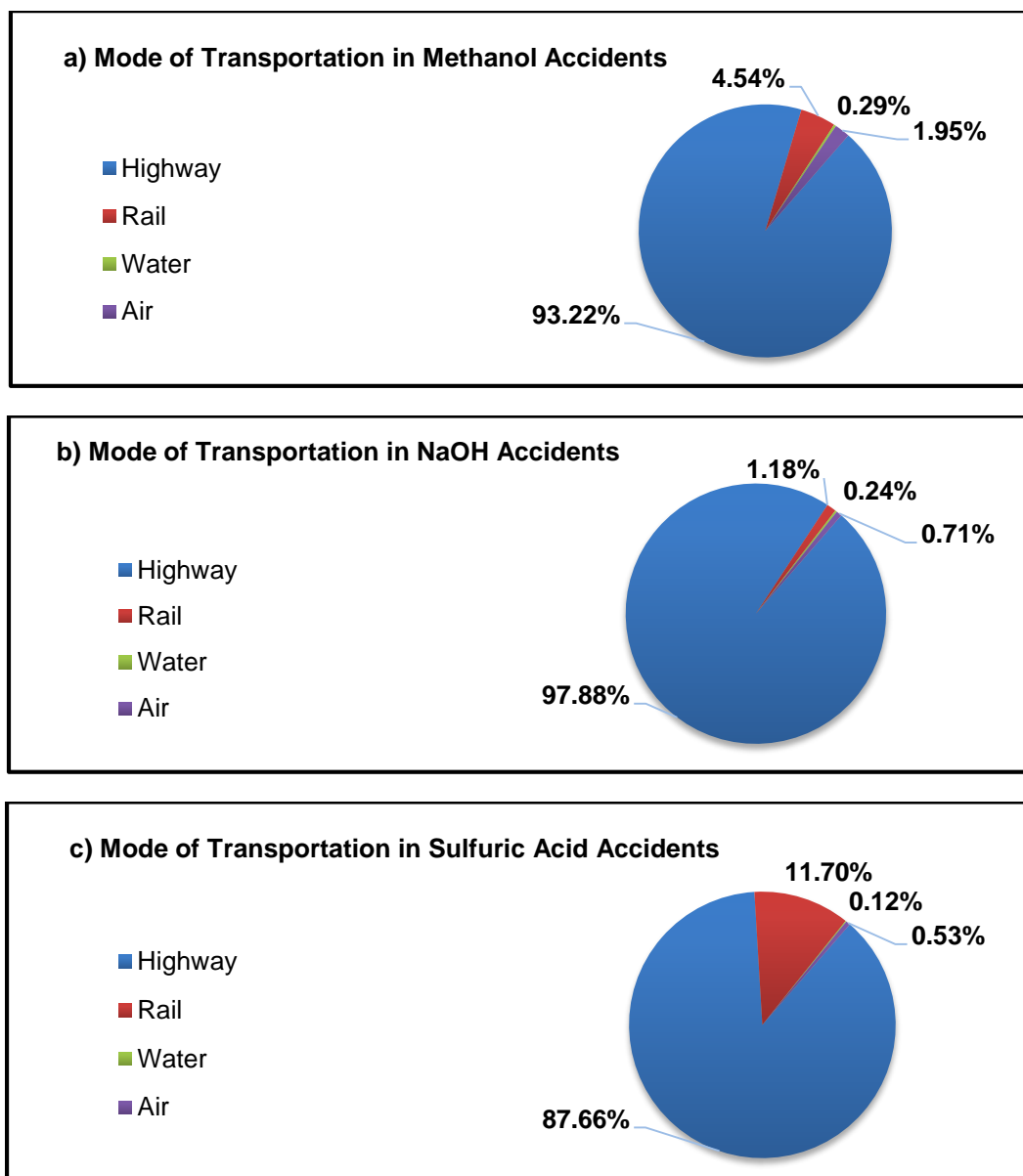


Fig. 5.2: Transportation mode during the accidents of each of the selected input chemicals to the biodiesel production over the period between 2006 and 2013.

It is also important to investigate in which transportation phase these accidents occur. Transportation phases describe the place of the incident occurrence in the transportation system. The process started with loading the chemical from the producing sites and then involving the transition to the final destination at which unloading takes place at another processing site, exporting site, or distribution locations.

According to the Guide for Preparing Hazardous Materials Incidents Reports published on 2004 by Pipeline and Hazardous Materials Safety Administration, U.S. Department of Transportation, “In transit” means that the incident happened or was first noticed during the process of transporting the package while “In-transit storage” is referred to the occurrence or discovering the incident in an in-transit storage area (e.g., a terminal or warehouse) while waiting for the upcoming leg of transportation.

Fig. 5.3 shows the transportation phase during the accidents of each of the selected input chemicals between 2006 and 2013. The data shows that unloading the chemicals is the dominant phase in which the majority of the accidents occurred followed by the loading and transferring the chemicals.

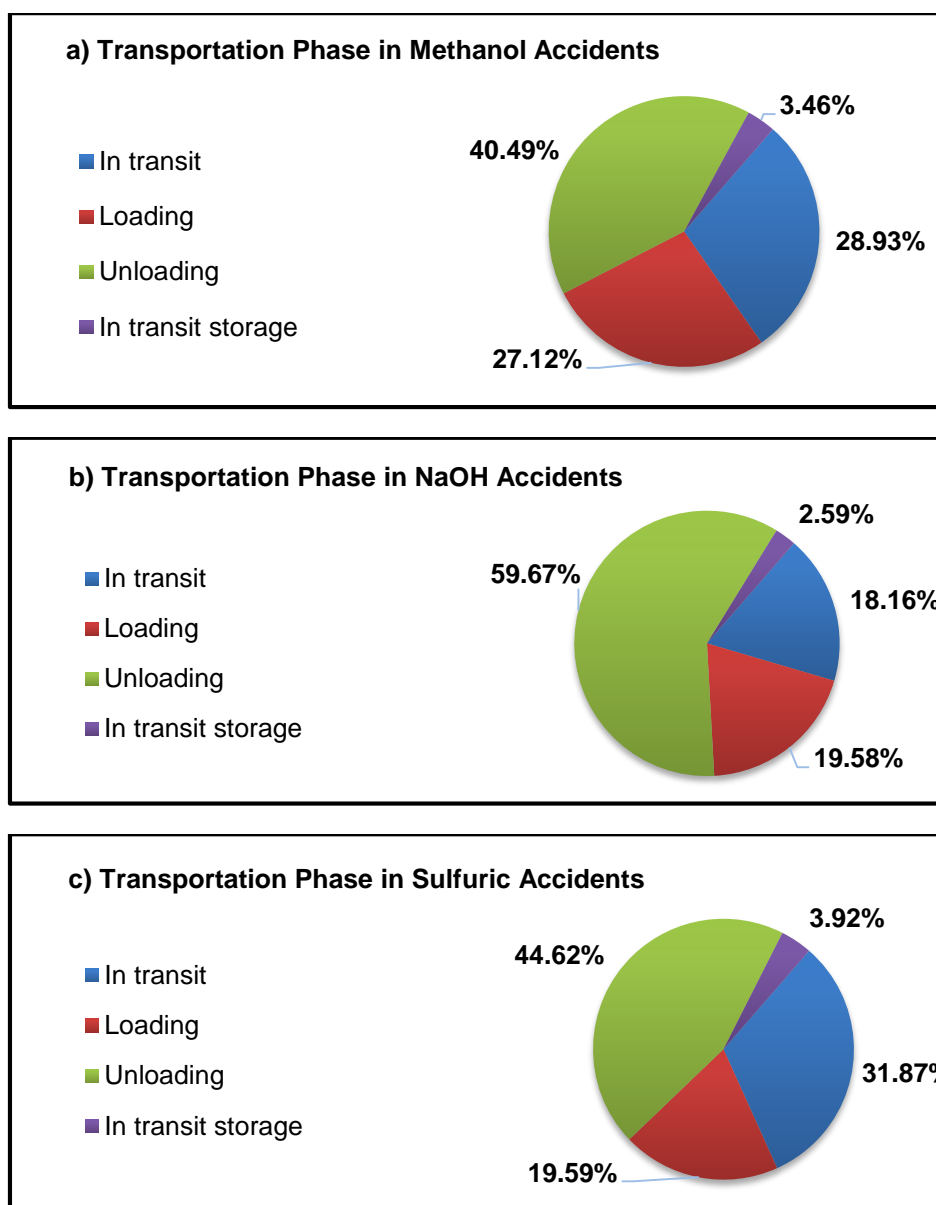


Fig. 5.3: Transportation phase during the accidents of each of the selected input chemicals to the biodiesel production over the period between 2006 and 2013.

In the event of an accident, several scenarios may occur resulting in different consequences of fatalities, injuries, or physical damage to surrounding machines, equipment, buildings, sites, or any other properties. The severity of the consequence depends on the type of the accident event noticed such as vapor gas dispersion, fire, explosion, and the possibility of the chemical to enter the nearby waterway or cause environmental damage. Therefore, by investigating the data, it is revealed that the spillage comprises 97-98% of the events in the accidents of each of the three selected chemicals. Also, when excluding the spillage, Figures 5.4-5.6 show that the dominant event type was vapor gas dispersion in methanol and sulfuric acid accidents.

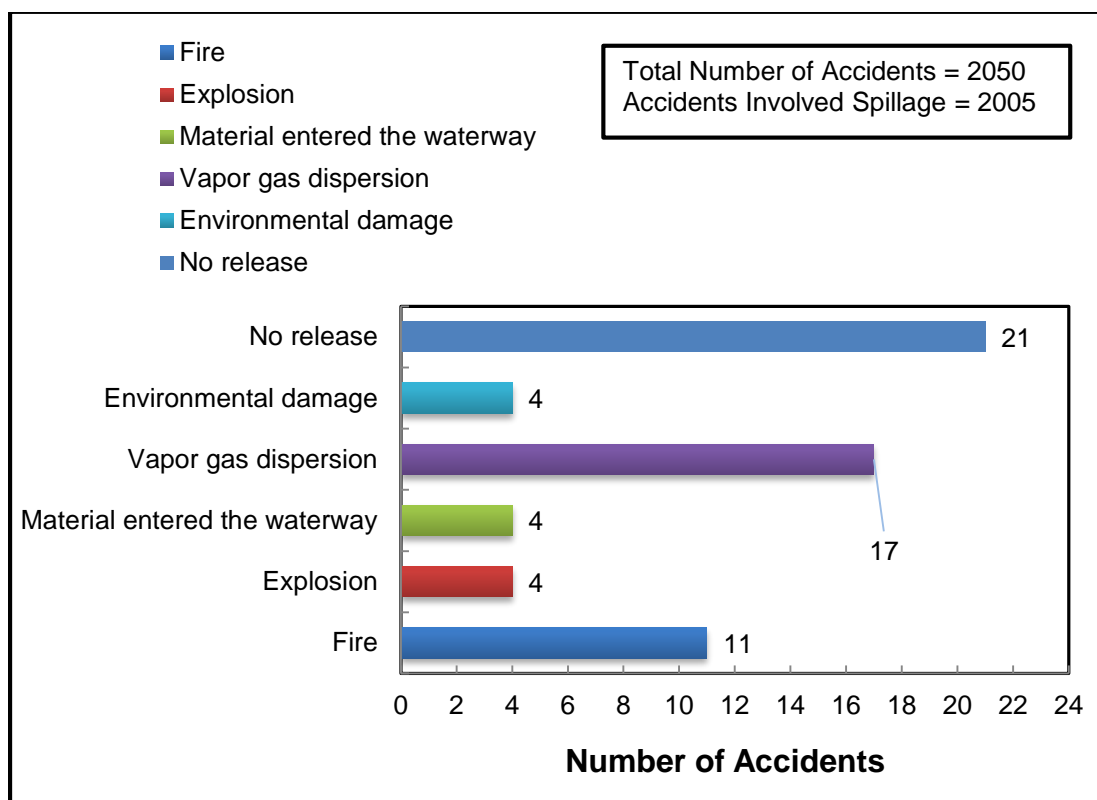


Fig. 5.4: Type of events in methanol transportation accidents from 2006 till 2013.

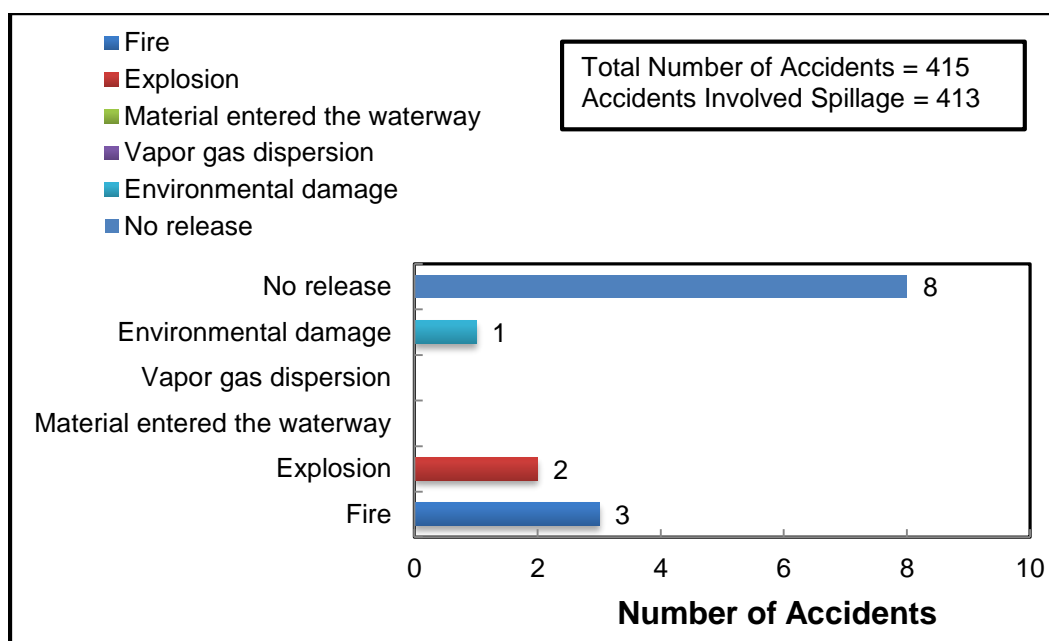


Fig. 5.5: Type of events in sodium hydroxide transportation accidents from 2006 till 2013.

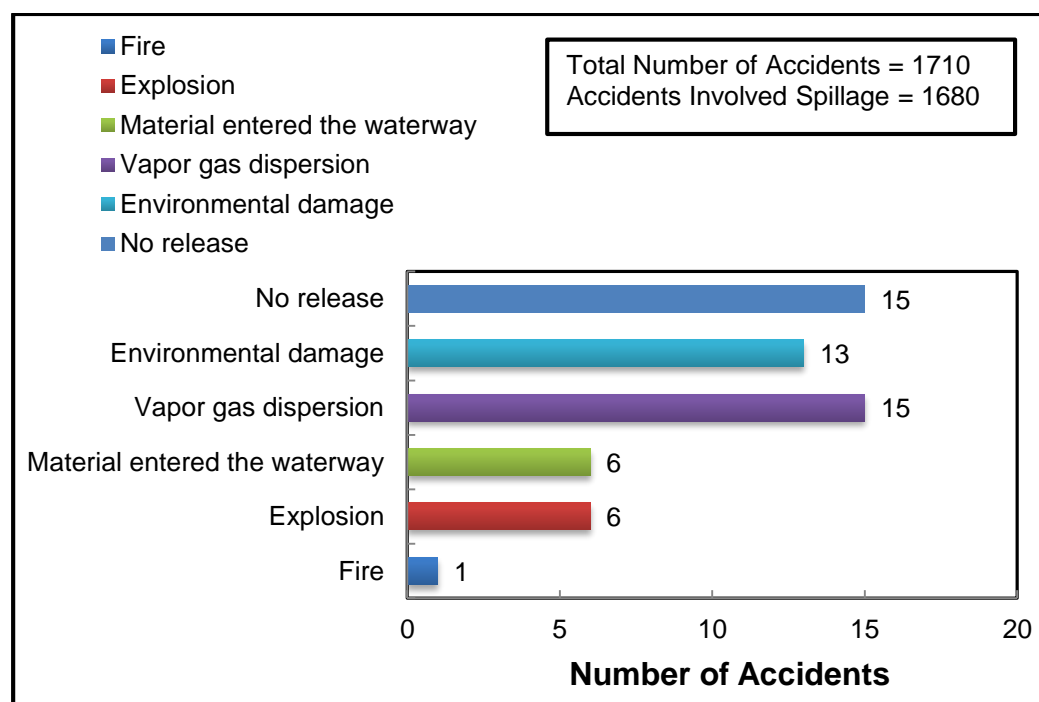


Fig. 5.6: Type of events in sulfuric acid transportation accidents from 2006 till 2013.

The data were used to analyze the causes of failure in the accidents associates with each chemical. This analysis is illustrated in **Fig. 5.7** through **Fig. 5.9**. Common causes included: dropping the chemical, failure of a component, improper or inadequate preparation for the transportation, overfilling, over pressuring, and human error.

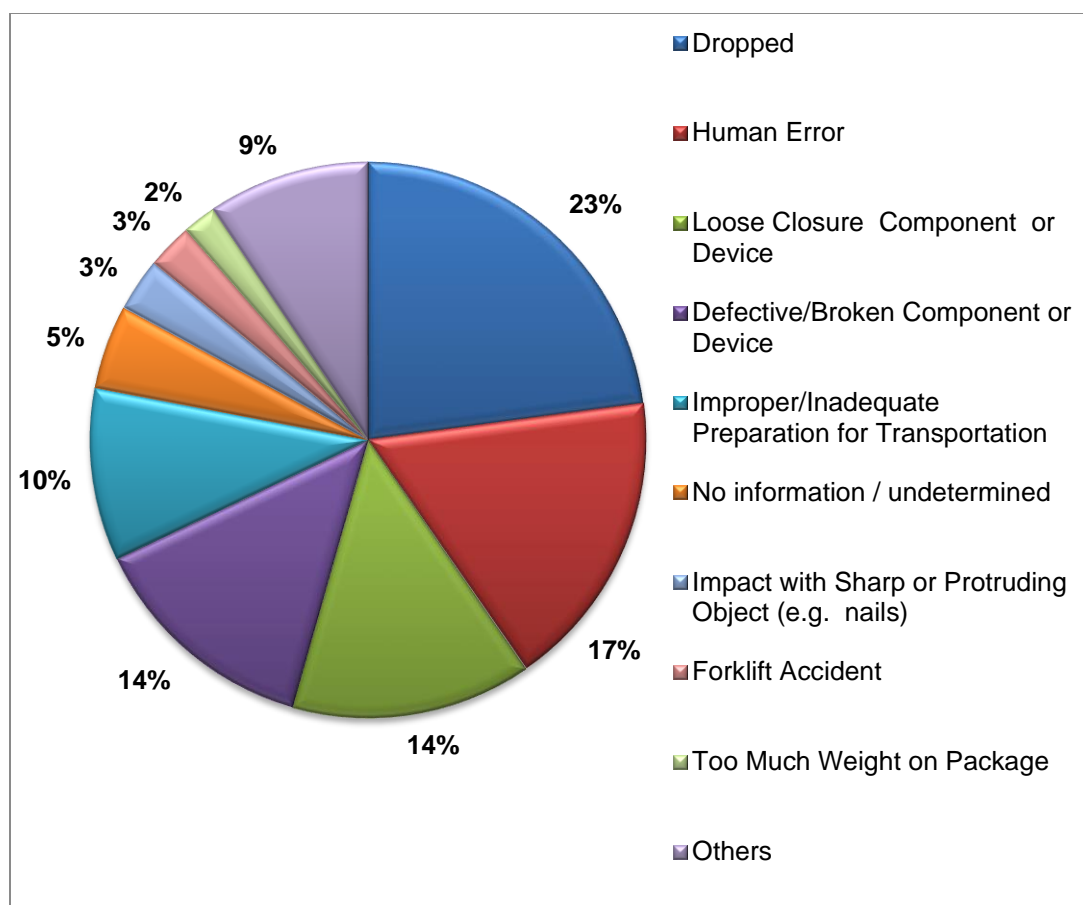


Fig. 5.7: Failure causes for methanol transportation accidents over the period between 2006 and 2013.

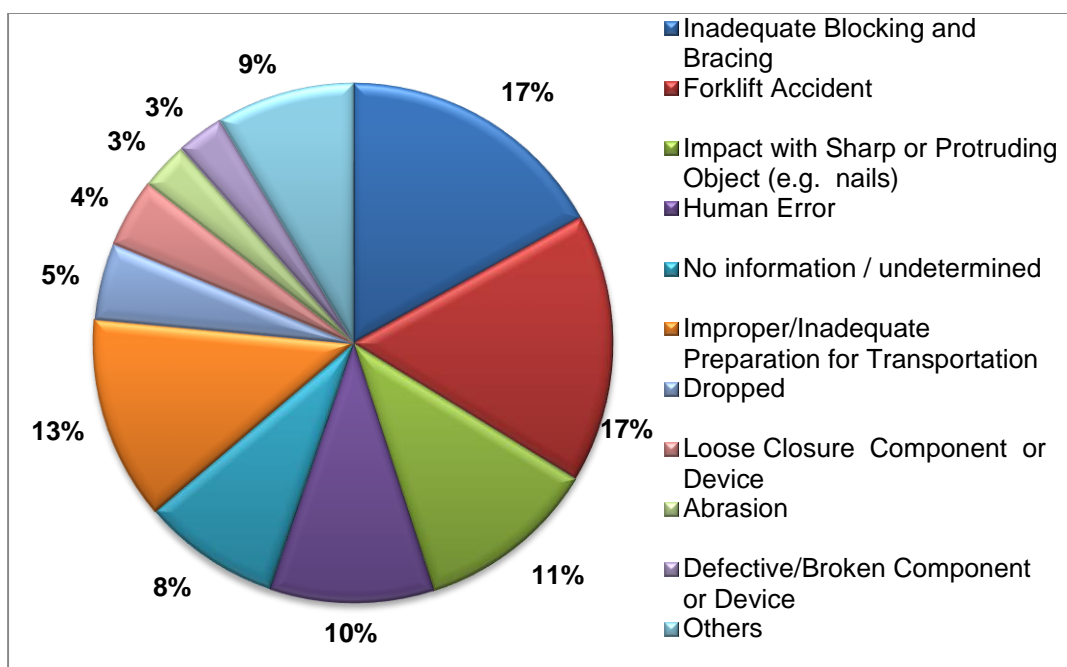


Fig. 5.8: Failure causes for sodium hydroxide transportation accidents from 2006 till 2013.

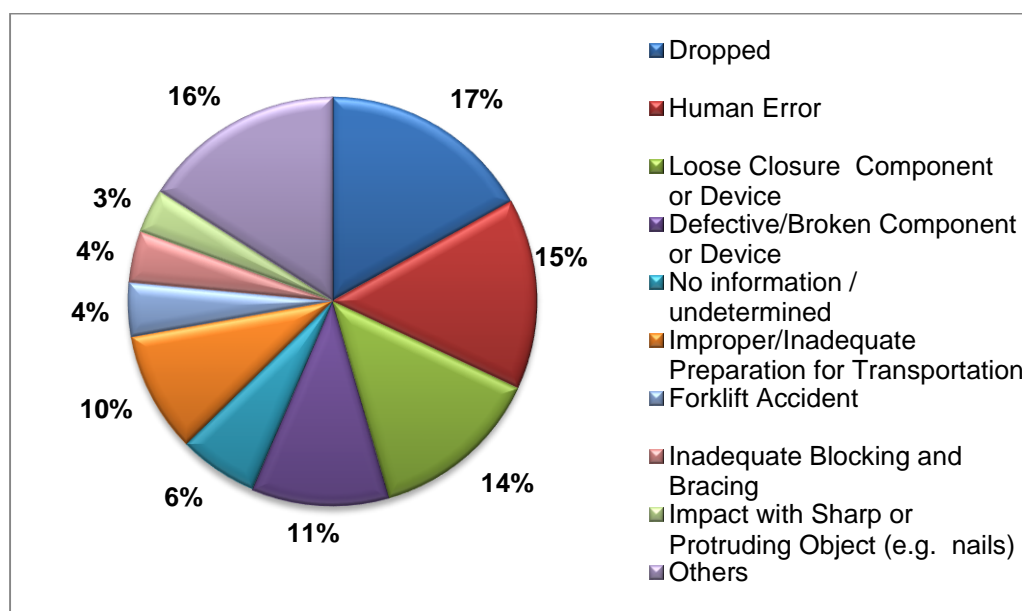


Fig. 5.9: Failure causes for sulfuric acid transportation accidents from 2006 till 2013.

5.2.2 Product

Diesel fuel was used as a representative for the biodiesel due to the lack of any data that reports the accidents in biodiesel transportation. **Figure 5.10-a** shows the number of accidents involved with diesel fuel transportation continues increasing in the number of accidents with diesel fuel.

Diesel fuel transportation mode and phase for diesel fuel are summarized in **Fig. 5.10-b** and **c** and, while **Fig. 5.11** illustrates the failure causes in these accidents and **Fig. 5.12** illuminates type of events resulted. Similar to was observed for the input chemicals, transportation by highways was the most dominant mode in these accidents. In addition, unloading still was the dominant phase.

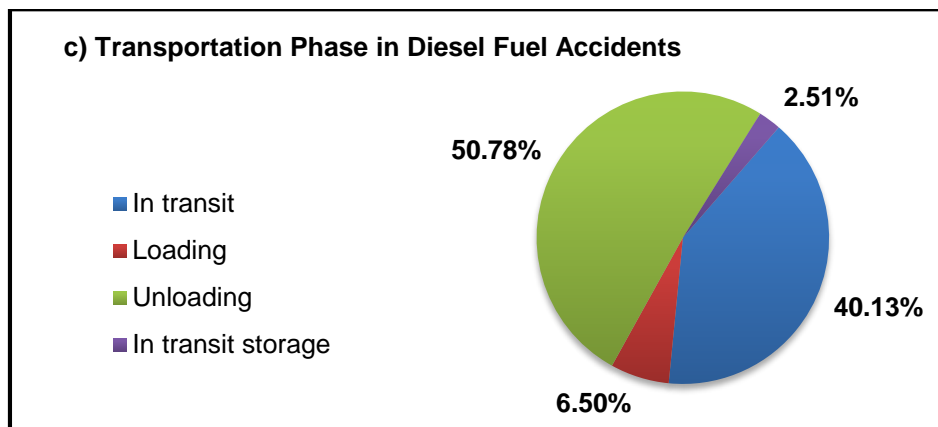
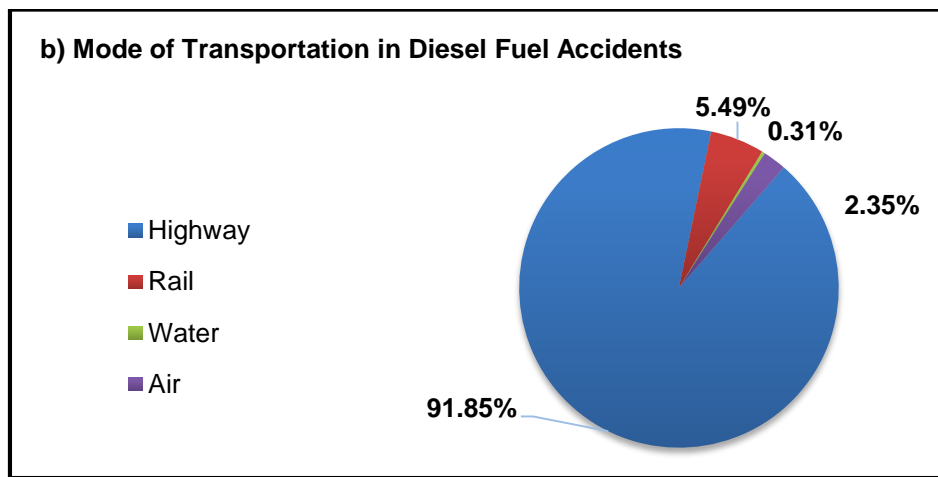
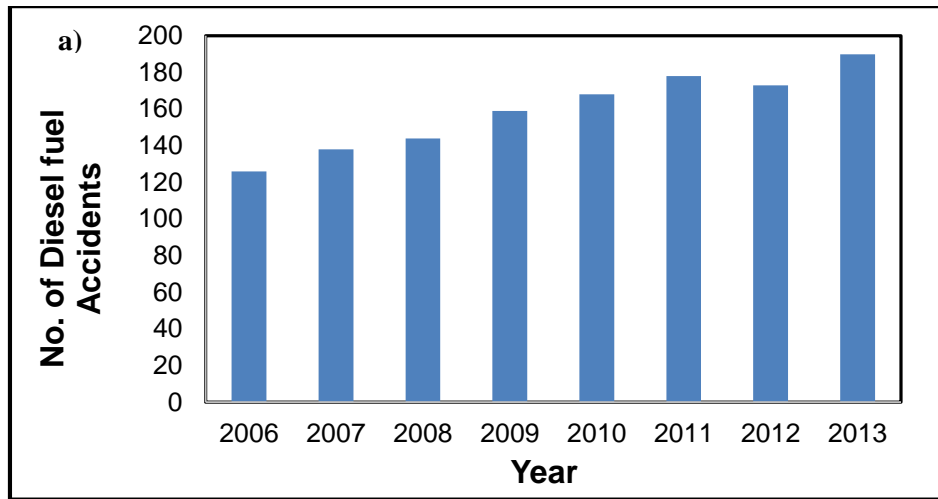


Fig. 5.10: Number of accidents, mode of transportation, and phase of transportation involved with diesel fuel transportation.

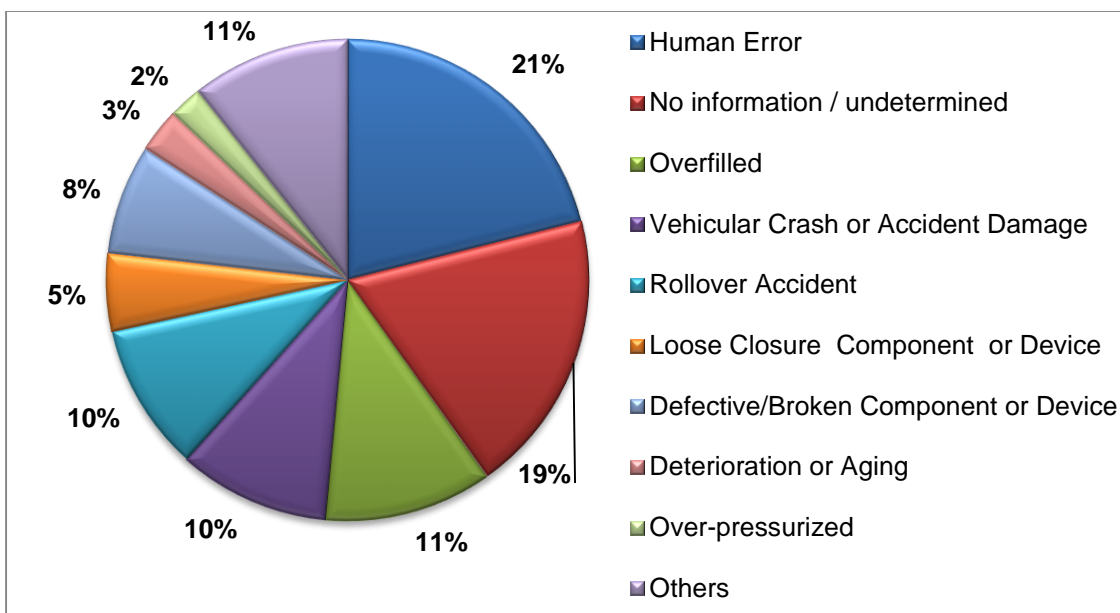


Fig. 5.11: Failure causes for diesel fuel transportation accidents from 2006 till 2013.

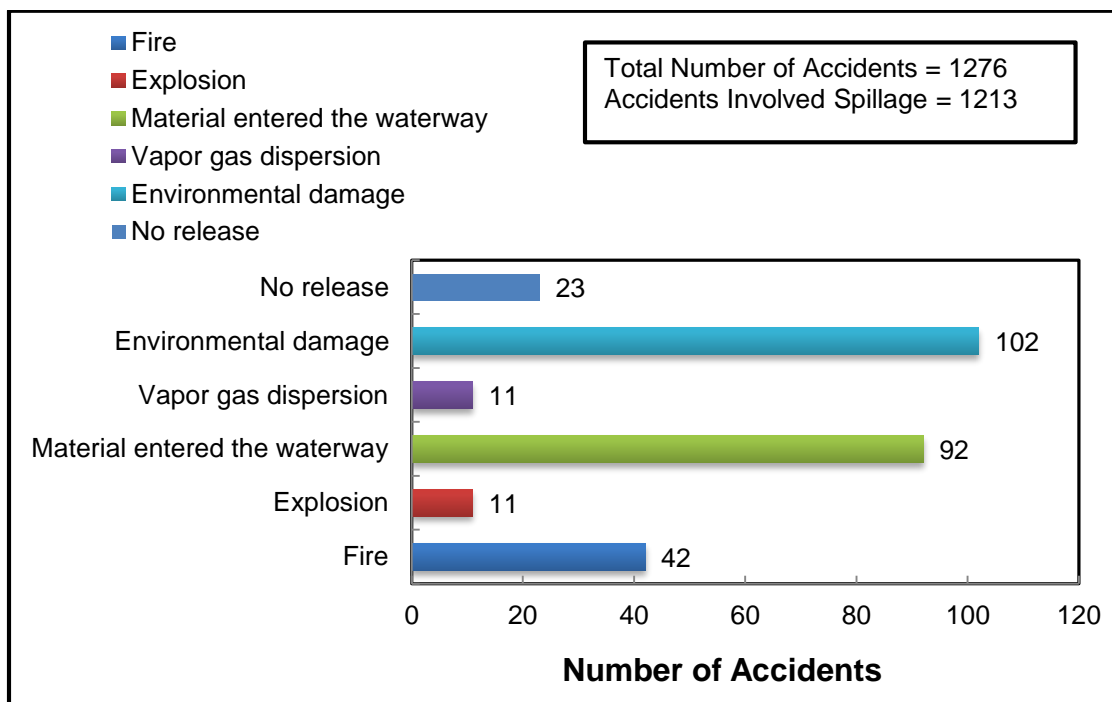


Fig. 5.12: Type of events in sulfuric acid transportation accidents from 2006 till 2013.

5.3 Risk Calculations

The objective of this section is to determine the risk associated with the transportation of biodiesel in the way it was calculated for the processes in plants as discussed in section 4. The data collected from the accidents occurred over the period between 2006 and 2013 was used to calculate the probability and the severity of several categories of consequence in each year. The consequences included the fatalities, major (hospitalized) injuries, minor (non-hospitalized) injuries, and physical damages to surrounding buildings, equipment, or properties that resulted in monetary losses.

Table 5.1 through **Table 5.3** shows the consequences of the selected input chemicals and diesel fuel over the investigated period of time. Data shows that transportation accidents of methanol and sodium hydroxide did not result in any significant fatalities. However, sulfuric acid resulted in just one fatality while diesel fuel did cause significant number of fatalities; around 92% of all fatalities resulted. Sulfuric acid and Diesel fuel contributed to the majority of the hospitalized injuries with percentages of 60% and 35% respectively from the overall. Regarding the non-hospitalized injuries, Sulfuric acid was involved in 80% of all non-hospitalized injuries resulted and sodium hydroxide affected around 13% of the injuries while methanol and diesel fuel contributed in 3.5% each.

Table 5.1: Number of fatalities resulted from the transportation accidents.

Year	Fatalities			
	Methanol	Sodium Hydroxide	Sulfuric Acid	Diesel Fuel
2006	0	0	0	2
2007	0	0	0	2
2008	0	0	0	1
2009	0	0	0	2
2010	0	0	0	2
2011	0	0	1	2
2012	0	0	0	0
2013	0	0	0	0
total	0	0	1	11

Table 5.2: Number of hospitalized injuries resulted from the transportation accidents.

Year	Hospitalized Injuries			
	Methanol	Sodium Hydroxide	Sulfuric Acid	Diesel Fuel
2006	0	0	1	2
2007	0	0	3	1
2008	0	0	2	0
2009	0	0	2	2
2010	0	0	1	0
2011	0	0	1	1
2012	0	0	1	0
2013	0	1	1	1
total	0	1	12	7

Table 5.3: Number of non-hospitalized injuries resulted from the transportation accidents.

Year	Non-Hospitalized Injuries			
	Methanol	Sodium Hydroxide	Sulfuric Acid	Diesel Fuel
2006	0	2	10	0
2007	0	1	7	0
2008	0	4	23	0
2009	1	2	13	1
2010	0	0	11	0
2011	3	6	3	0
2012	0	0	16	2
2013	0	0	9	1
total	4	15	92	4

5.3.1 Quantitative Risk Calculations

This section explains how the probability and the risk of each consequence resulted from the transportation accidents were determined. For each selected chemical, the probability and the risk of a certain consequence (fatalities, injuries, damage) at a specific year were determined in two different units (\$/accident and \$/amount transported) as follows:

Risk of each category of consequence per accident per year

$$\begin{aligned} \text{Risk of consequence/ Accident . year} \\ = P(\text{Consequence})/ \text{Accident . year} \times \text{Magnitude of consequence} \end{aligned} \quad (5.1)$$

Where,

$$P(\text{Consequence}) / \text{Accident} \cdot \text{year} = \left(\frac{\text{Number of Consequence}}{\text{Number of accidents}} \right)_{\text{year}} \quad (5.2)$$

The total risk in each year is calculated as follows:

Total risk in specific year =

$$\begin{aligned} & \text{Risk of fatality} + \text{Risk of major injury} + \text{Risk of minor injury} \\ & + \text{Risk of major damage} + \text{risk of minor damage} \end{aligned} \quad (5.3)$$

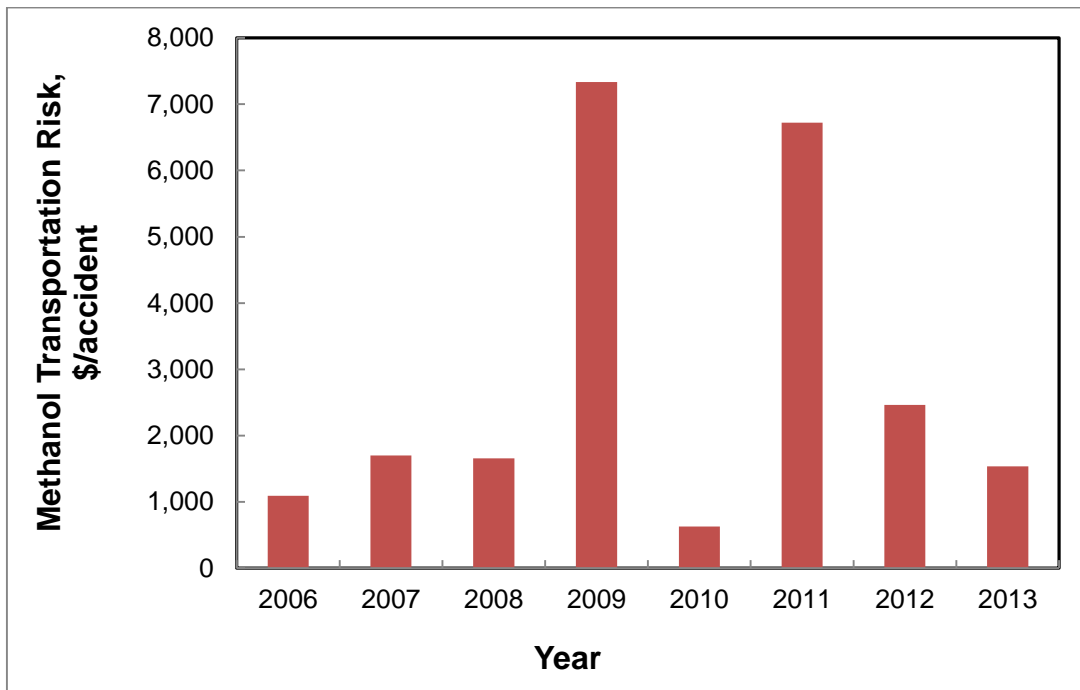


Fig. 5.13: Risk per accident of methanol transportation in the U.S. from 2006 till 2013.

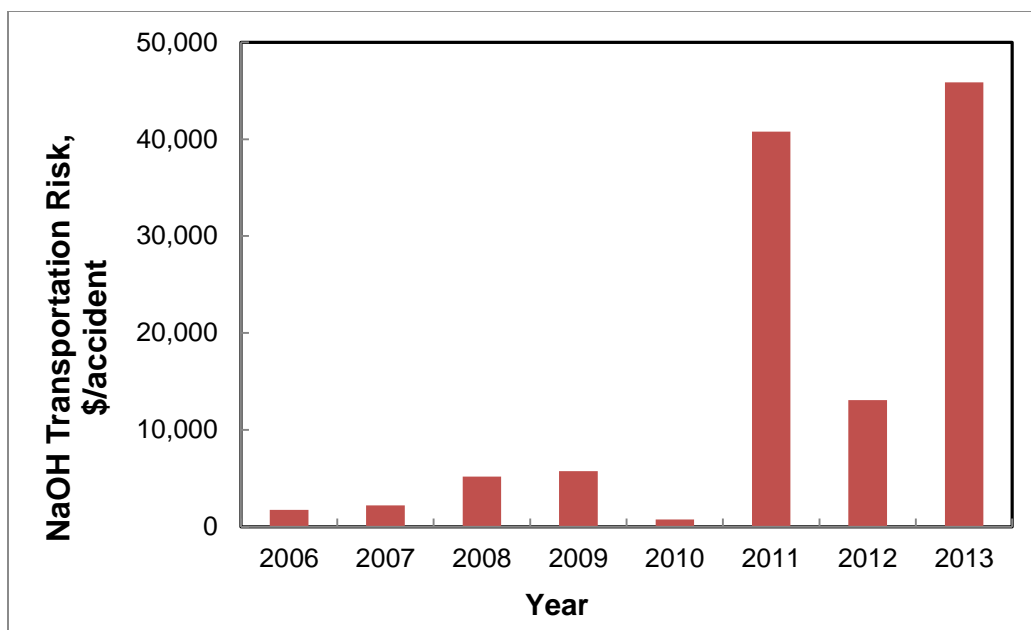


Fig. 5.14: Risk per accident of sodium hydroxide transportation in the U.S. from 2006 till 2013.

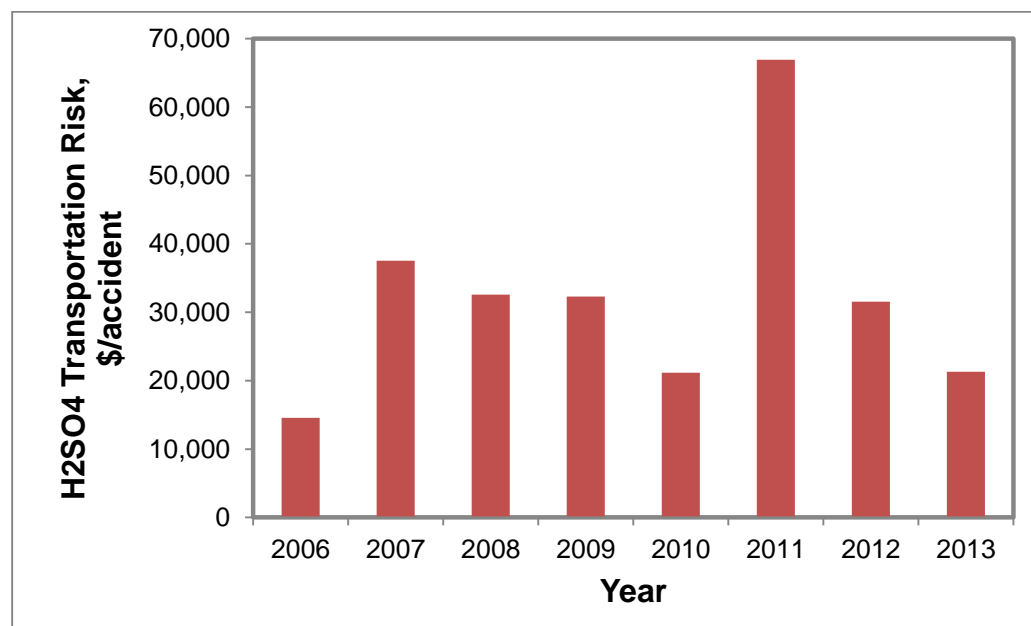


Fig. 5.15: Risk per accident of sulfuric acid transportation in the U.S. from 2006 till 2013.

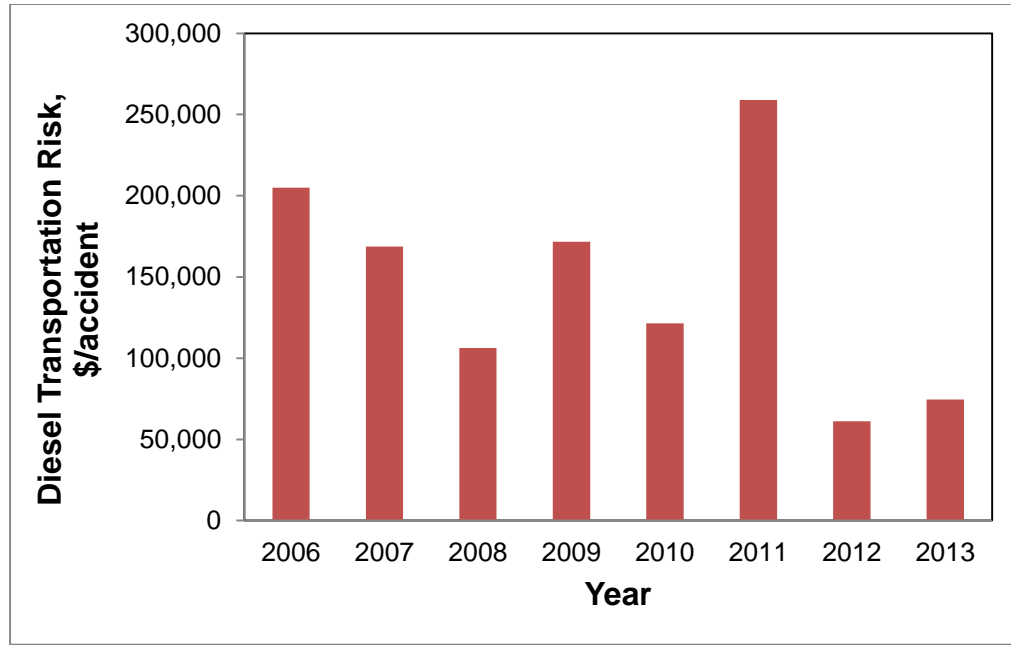


Fig. 5.16: Risk per accident of diesel transportation in the U.S. from 2006 till 2013.

Risk of each category of consequence per amount of material transported per year

$$\begin{aligned} &\text{Risk of consequence/material transported} \cdot \text{year} \\ &= P(\text{Consequence})/\text{material transported} \cdot \text{year} \times \text{Magnitude of consequence} \end{aligned} \quad (5.4)$$

Where,

$$P(\text{Consequence})/\text{material transported} \cdot \text{year} = \left(\frac{\text{Number of Consequence}}{\text{amount of material transported}} \right)_{\text{year}} \quad (5.5)$$

Where,

$P(\text{Consequence})/\text{material transported} \cdot \text{year}$: Probability of consequence per amount of material transported at certain year

It is assumed here that the amount of material transported, whether it has been resulted in accidents or not, is equal to the amount of material produced (USITC, 1995; Evans, 2011; U.S. Census, 2012) due to lack of sufficient data regarding the total amount transported. It worth noting that there is a strong need for reporting the amount of materials

that are not involved in accidents also; because that will give more broader view of how much of the total material transported is employed in accidents and/or causing problems.

Then total risk can be calculated as in equation (5.3)

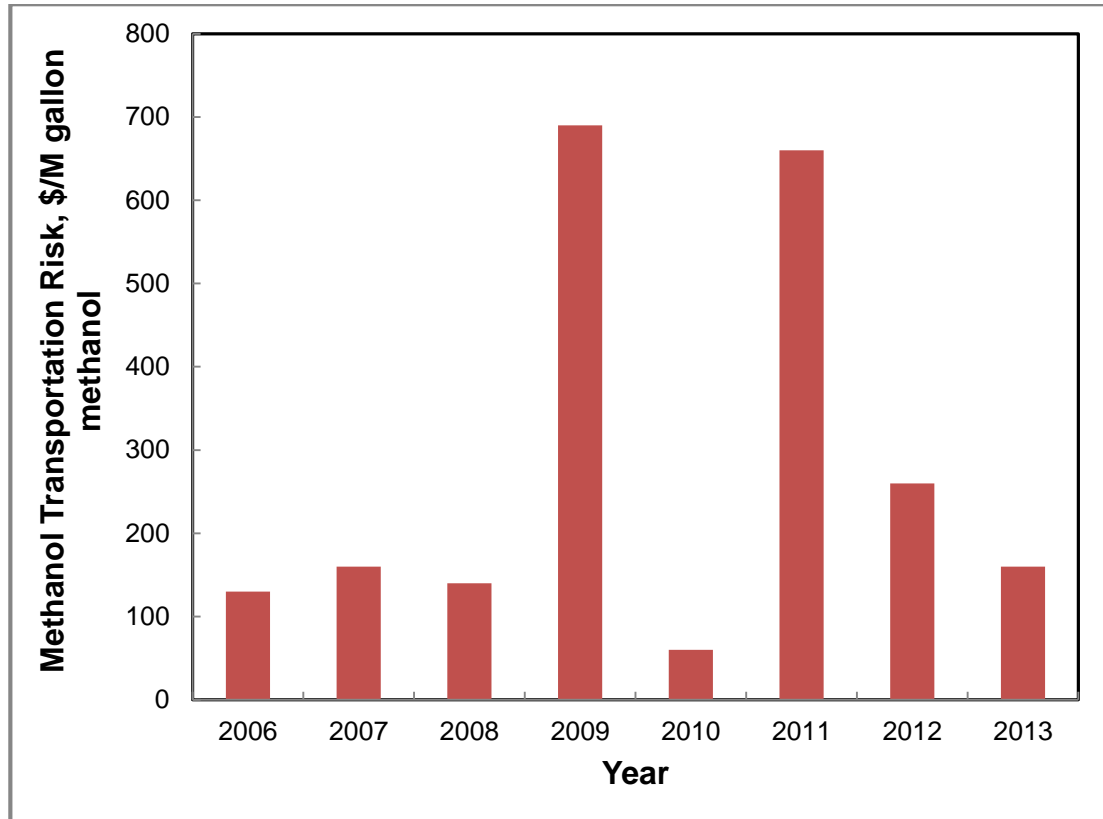


Fig. 5.17: Risk per amount of methanol transportation in the U.S. from 2006 till 2013.

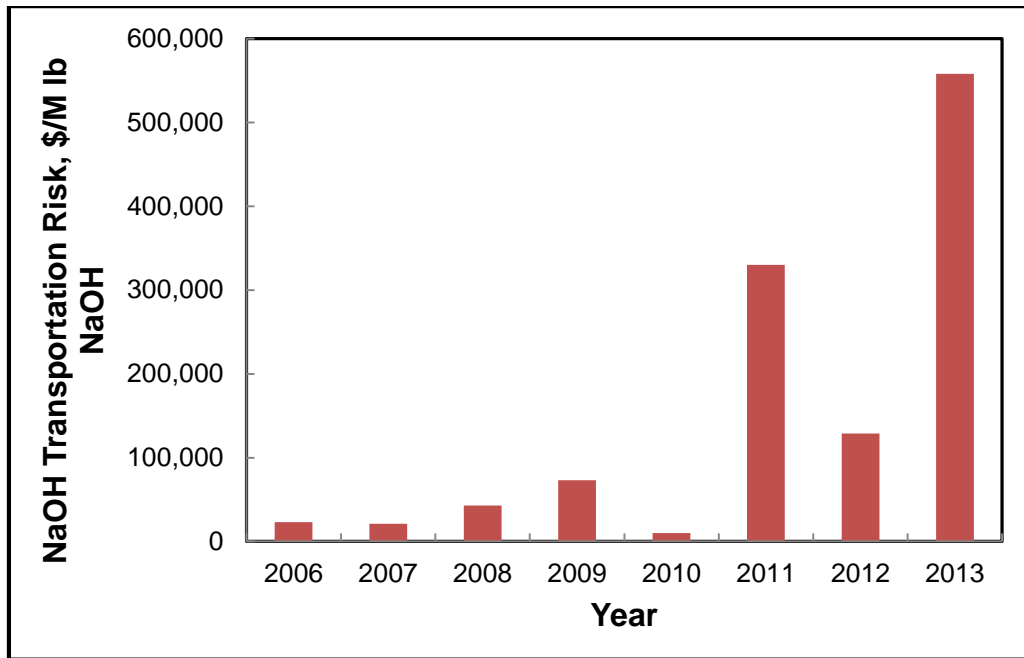


Fig. 5.18: Risk per amount of sodium hydroxide transportation in the U.S. from 2006 till 2013.

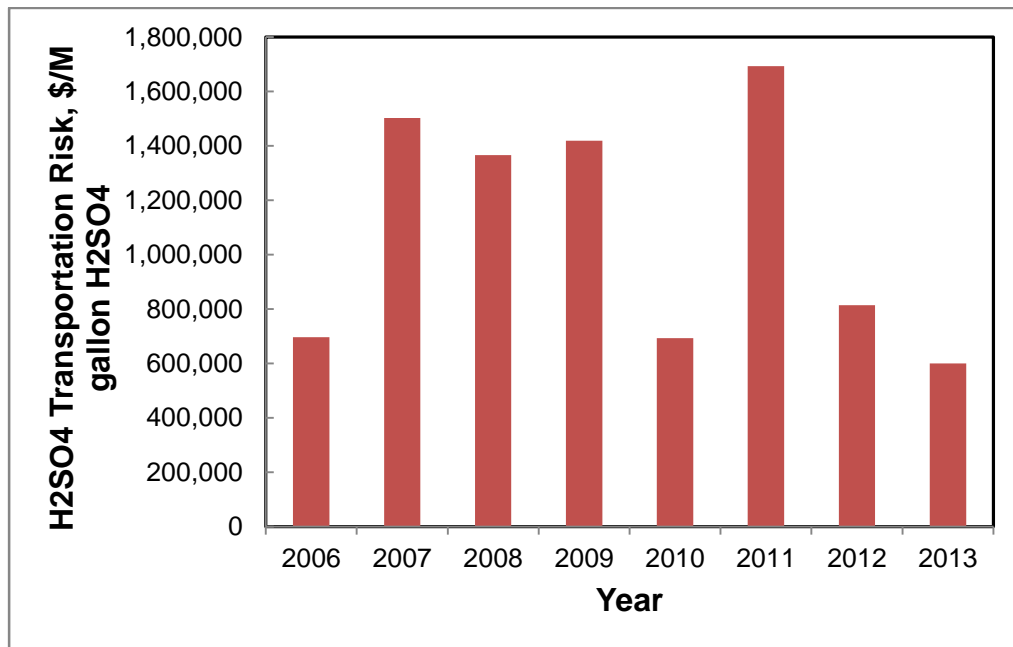


Fig. 5.19: Risk per amount of sulfuric acid transportation in the U.S. from 2006 till 2013.

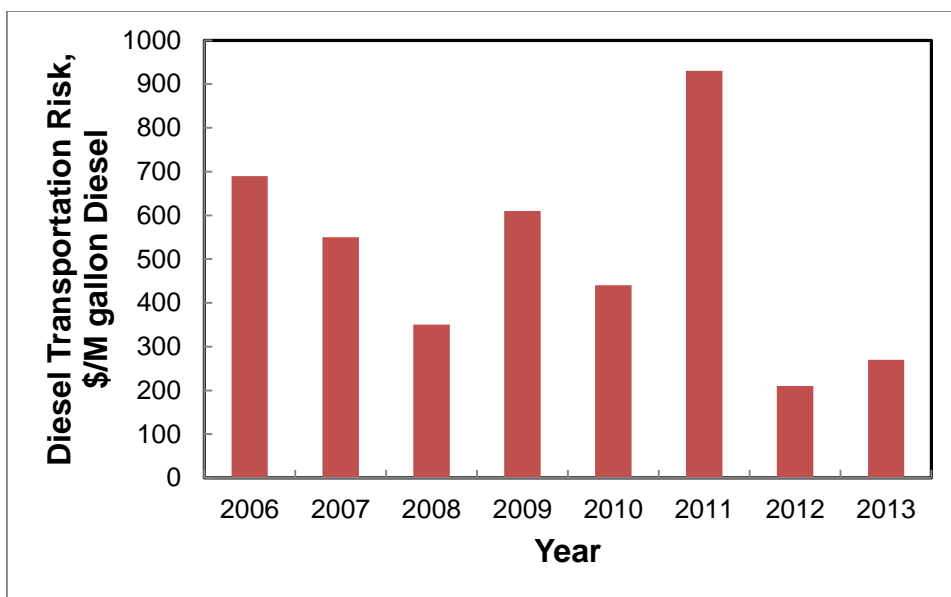


Fig. 5.20: Risk per amount of diesel transportation in the U.S. from 2006 till 2013.

5.3.2 Semi-quantitative Risk Matrix

A semi-quantitative risk matrix addressing the risk level of each of the selected chemical was constructed as a function of time based on the frequency and the level of severity of the consequences each year. The probability used was determined as follows:

$$P(\text{Accident})/\text{year} = \left(\frac{\text{Chemical amount transported during accidents}}{\text{Total chemical amount transported}} \right)_{\text{year}} \quad (5.6)$$

Where,

$P(\text{Accident})/\text{year}$: Probability of occurrence of an accident at certain year

The accident reported data was used to determine the level of severity of the accidents associated with each chemical. The results are discussed below.

The frequency of the methanol accidents follows a single category, category D (or the remote), which is set when the $10^{-6} \leq \text{Probability of occurrence} < 10^{-3}$. Sodium Hydroxide also follows a single category of probability (B, or probable). Category of the frequency of sulfuric acid accidents was mixed between “A, frequent” and “B, probable”. Diesel fuel accidents fell into the remote and occasional categories. **Table 5.4** summarizes these results.

Table 5.4: The frequency (probability) of the consequences associated with the transportation accidents.

Year	Probability Level			
	Methanol	Sodium Hydroxide, Solid	Sulfuric Acid	Diesel Fuel
2006	Remote	Probable	Probable	Remote
2007	Remote	Probable	Probable	Occasional
2008	Remote	Probable	Probable	Remote
2009	Remote	Probable	Frequent	Remote
2010	Remote	Probable	Frequent	Remote
2011	Remote	Probable	Frequent	Remote
2012	Remote	Probable	Probable	Occasional
2013	Remote	Probable	Probable	Remote

The levels of severity of these selected chemicals are shown in **Table 5.5**. The data collected from the accidents revealed that methanol and sodium hydroxide fell in the levels

from negligible to critical. Sulfuric acid and diesel fuel, however, showed a single level of “catastrophic” over the investigated period between 2006 and 2013.

Table 5.5: The severity level of the consequences associated with the transportation accidents.

Year	Severity Level			
	Methanol	Sodium Hydroxide, Solid	Sulfuric Acid	Diesel Fuel
2006	Marginal	Marginal	Catastrophic	Catastrophic
2007	Marginal	Negligible	Catastrophic	Catastrophic
2008	Marginal	Marginal	Catastrophic	Catastrophic
2009	Critical	Marginal	Catastrophic	Catastrophic
2010	Marginal	Negligible	Catastrophic	Catastrophic
2011	Critical	Critical	Catastrophic	Catastrophic
2012	Marginal	Marginal	Catastrophic	Catastrophic
2013	Marginal	Marginal	Catastrophic	Catastrophic

Based on both the probability and the severity levels, a risk profile for each chemical can be allocated in the risk matrix for each year as shown in **Table 5.6**. Sulfuric acid, unexpectedly, showed the highest level of risk even more than diesel fuel. This is due to both of the high probability and frequency of the accidents and the level of severity

over the investigated period. Sodium hydroxide, although showed a moderate severity level, the high probability levels resulted in high risk level.

Table 5.6: The Risk level of the consequences associated with the transportation accidents.

Year	Risk Level			
	Methanol	Sodium Hydroxide, Solid	Sulfuric Acid	Diesel Fuel
2006	Medium	Serious	High	Serious
2007	Medium	Medium	High	High
2008	Medium	Serious	High	Serious
2009	Medium	Serious	High	Serious
2010	Medium	Medium	High	Serious
2011	Medium	High	High	Serious
2012	Medium	Serious	High	High
2013	Medium	Serious	High	Serious

6. OVERALL RISK ANALYSIS IN THE U.S. BIODIESEL INDUSTRY

In this section, the overall risk associated with the biodiesel industry is discussed for the United States over the period between 2006 and 2013. The life cycle principle was applied to consider the contributing risk carried into this industry from the input chemicals and through the variant phases including the transportation and the process. First, the different consequences either related to the transportation and the process is addressed. Afterwards, the risk matrix is constructed and analyzed.

6.1 Data Analysis

The consequence of fatalities from both phases of biodiesel industry (plant and transportation) is shown in **Table 6.1**. It is quite interesting to observe that the transportation of the product (here diesel fuel is representing biodiesel) was associated with number of fatalities which is more than twice the number from the plant. This shows that chemical processes might be safer than many of other activities that seem to be safe by default.

Table 6.2 and **Table 6.3** illustrates the number of major (hospitalized) and the minor (non-hospitalized), respectively. Data indicates that the transportation of the selected input chemicals resulted in significant consequences which can be either very close to (for hospitalized) or exceed (for non-hospitalized) those resulted from the plant.

Table 6.1: Number of fatalities resulted from biodiesel plants and biodiesel transportation over the period between 2006 and 2013.

Year	Transportation of Input Chemicals	Plant	Product Transportation
2006	0	1	2
2007	0	1	2
2008	0	2	1
2009	0	0	2
2010	0	0	2
2011	1	0	2
2012	0	1	0
2013	0	0	0
Total	1	5	11

Table 6.2: Number of hospitalized injuries resulted from biodiesel plants and biodiesel transportation over the period between 2006 and 2013.

Year	Transportation of Input Chemicals	Plant	Product transportation
2006	1	1	2
2007	3	1	1
2008	2	4	0
2009	2	4	2
2010	1	2	0
2011	1	0	1
2012	1	0	0
2013	2	0	1
Total	13	12	7

In addition, the cost of the damage resulted from the transportation of the product was always higher than what resulted from the plant accidents, as shown in **Fig. 6.1**.

Table 6.3: Number of non-hospitalized injuries resulted from biodiesel plants and biodiesel transportation over the period between 2006 and 2013.

Year	Transportation of Input Chemicals	Plant	Product transportation
2006	12	1	0
2007	8	0	0
2008	27	4	0
2009	16	19	1
2010	11	3	0
2011	12	3	0
2012	16	2	2
2013	9	1	1
Total	111	33	4

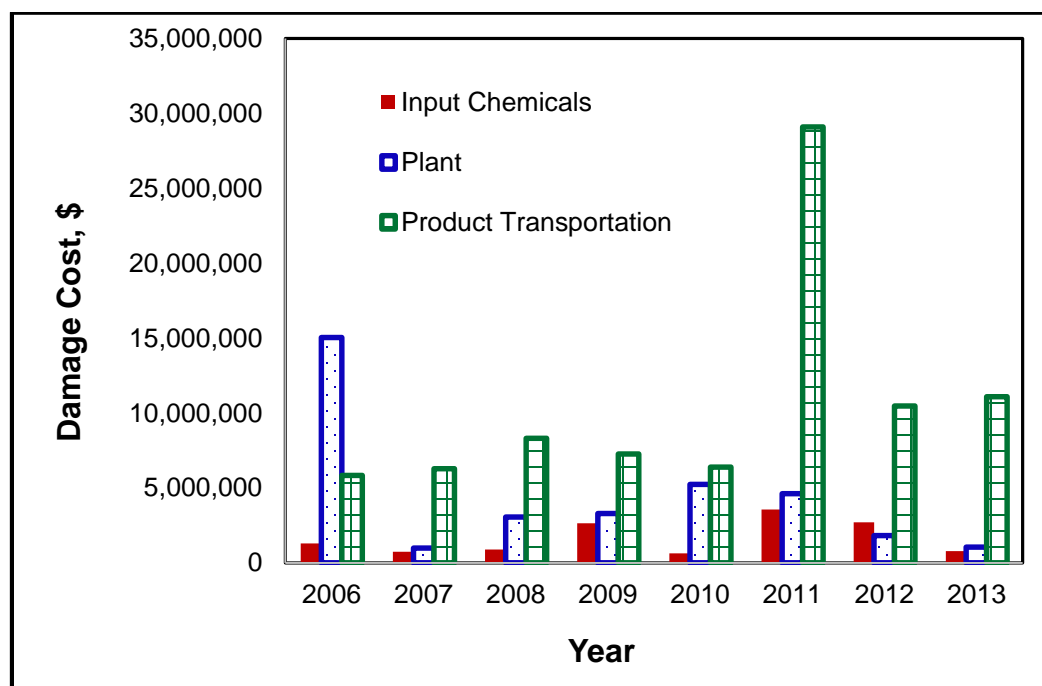


Fig. 6.1: Cost of damage resulted from the accidents in biodiesel transportation and processing over the period between 2006 and 2013.

6.2 Overall Risk Calculations

In this section, the risk resulted from the biodiesel transportation and processing in plants over the investigated period will be combined to determine the overall risk in quantitative and semi-quantitative approaches. From the latter, a risk matrix that describes the risk level of the biodiesel industry will be demonstrated.

6.2.1 Quantitative Risk Calculations

Revising the risk calculations in sections four and five, an important point has to be clarified, which is the difference in normalization used in each calculation. In this section, the risk in the biodiesel plants was normalized by the annual production volume of biodiesel; however the normalization in section five for the risk in the transportation was normalized by annual production volume of each chemical involved in the transportation accidents due to the lack of the data for total amount transported. Therefore, a mass targeting approach was used to convert the normalization in the risk transportation calculations to a basis of biodiesel production.

The mass targeting approach is a method in which the mass balance is used to determine the relative amounts of chemicals (input, product, byproducts) with respect to a selected reference (usually one of the products). The process requirements or specifications can also be used to determine the necessary amount of other materials such as catalysts or utilities per a basis amount of the selected reference.

Data from literature, which focused on simulation studies of the biodiesel processes, were used to determine the relative amount of each selected input chemical to

basis of biodiesel mass. **Table 6.4** and **Table 6.5** summarizes the results of 8 simulation studies and shows the quantities used from the raw material (different types of oil), the biodiesel produced, and the corresponding input chemicals and catalysts.

These data was used to determine the average of the ratio of biodiesel produced to each of these chemicals used as an input to the process, as illustrated in **Table 6.6**. The later quantity was then applied to the risk calculations in the transportation to convert the normalization to a basis of biodiesel volume production.

Table 6.4: Summary of amount of input chemicals and products in biodiesel processing,
(part 1/2).

Reference Chemical	(Myint and El-Halwagi, 2009)	(Glisic and Skala, 2009)	(West et al., 2008)	(Jeerawongsuntorn et al., 2011)
Oil	Soybean 37,277 lb/hr	Pure oil 1,307 kg/hr	Waste oil 1,050 kg/hr	Soybean 1000 kg/hr
NaOH	372 lb/hr	10.45 kg/hr	10 kg/hr	12 kg/hr
Methanol	8,106 lb/hr	140.99 kg/hr	20.6 kg/hr	130 kg/hr
H ₂ SO ₄	-----	-----	10 kg/hr	-----
Biodiesel	36323.39 lb/hr	1208.6 kg/hr	1,001.8 kg/hr	1,002 kg/hr

Table 6.5: Summary of amount of input chemicals and products in biodiesel processing, (part 2/2).

Reference Chemical	(Rincón et al., 2014)		(Patle et al., 2014)	(Morais et al., 2010)
Oil	a) Palm oil 992.59 kg/hr	b) Jatropha oil 990.41 kg/hr	Waste oil 15,000 kg/hr	Waste oil 1,042.25 kg/hr
NaOH	9.33 kg/hr	9.51 kg/hr	141 kg/hr	9.80 kg/hr
Methanol	159.02 kg/hr	212.69 kg/hr	1,768.51 kg/hr	126.80 kg/hr
H ₂ SO ₄	20.84 kg/hr	21.24 kg/hr	90 kg/hr	-----
Biodiesel	1,000 kg/hr	1,000 kg/hr	15,167.3 kg/hr	1,000 kg/hr

Table 6.6: Ratio of biodiesel to each of the selected input chemicals used.

Reference	Gal Biodiesel / lb NaOH	Gal Biodiesel / Gal Methanol	Gal Biodiesel / Gal H ₂ SO ₄
(Myint and El-Halwagi, 2009)	13.4	4	---
(Glisic and Skala, 2009)	15.9	7.7	---
(West et al., 2008)	13.8	6.6	211
(Jeerawongsuntorn et al., 2011)	11.9	7.2	---
(Rincón et al., 2014) a)	14.8	5.7	101
(Rincón et al., 2014) b)	14.4	4.2	99
(Patle et al., 2014)	14.8	7.7	356
(Morais et al., 2010)	14	7.1	---
Average	14.1	6.3	192

Now the total risk of the biodiesel industry involving both the transportation and the processing can be determined as a function of time, as depicted in **Fig. 6.2**. The percentage of contribution towards the total risk from each phase as a function of time is shown in **Table 6.7**.

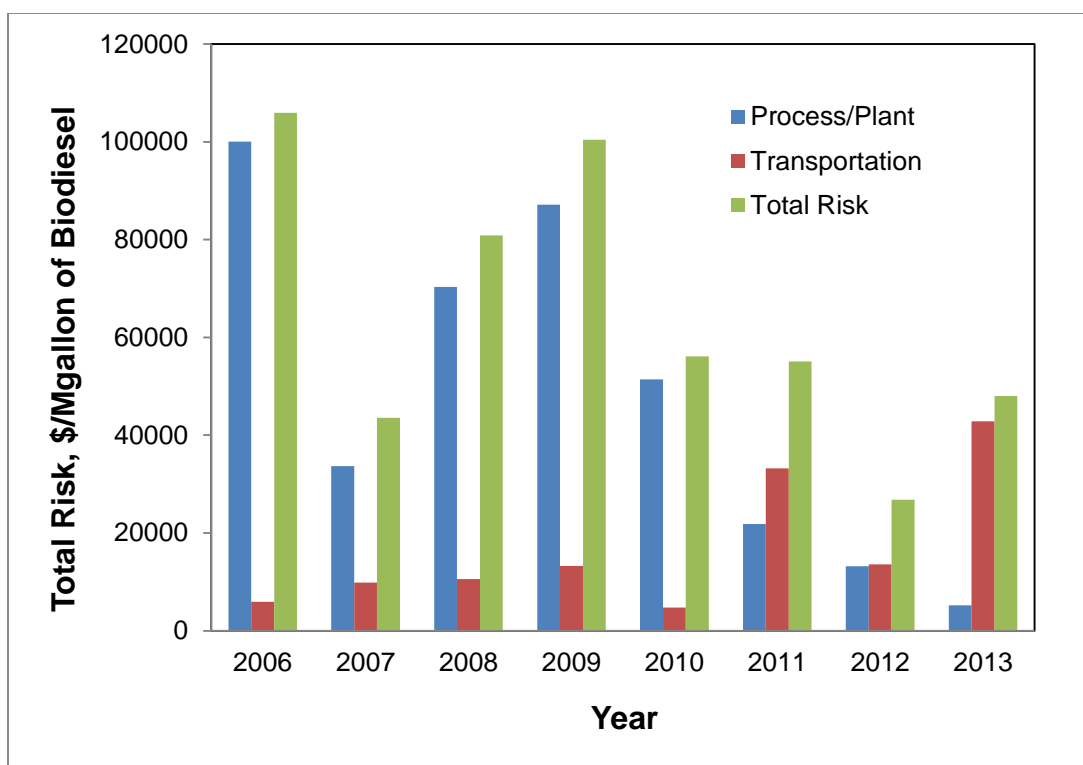


Fig. 6.2: Total risk of biodiesel industry based on life-cycle approach from 2006 till 2013.

Table 6.7: Percentage contribution of plants and transportation to total risk in the biodiesel industry over the period between 2006 and 2013.

Year	Transportation Contribution to total risk, %	Plants Contribution to total risk, %
2006	5.6	94.4
2007	22.7	77.3
2008	13.1	86.9
2009	13.2	86.8
2010	8.5	91.5
2011	60.3	39.7
2012	50.7	49.3
2013	89.2	10.8

6.2.2 Estimated Loss Based on Overall Risk Calculation

As mentioned before, total risk quantitative calculations are used to obtain a number that can be a representative to the whole risk per production amount; which can be utilized afterwards to anticipate the upcoming loss from the capacity increase. Based on the results of overall risk calculations, the potential loss resulted from accidents occurred during input chemicals transportation, input chemicals storage, production of the biodiesel, product storage, or product transportation over the period from 2006 to 2013 in United States is estimated as shown in **Table 6.8**. It worth noting that, the total estimated loss over the studied period was around 320 million dollars. These estimations are used to get an average number of the total risk, which can be used subsequently to anticipate the upcoming loss in upcoming years as shown in **Table 6.9**.

Table 6.8: Estimation of the resulted loss based on total risk in the biodiesel industry over the period between 2006 and 2013.

Year	US Production, M gal	Total Risk, \$/M gal	Estimated loss, \$
2006	250.439	105,971	26,540,000
2007	489.825	43,569	21,340,000
2008	678.106	80,900	54,860,000
2009	515.805	100,422	51,800,000
2010	343.445	56,148	19,280,000
2011	967.481	55,069	53,280,000
2012	990.711	26,825	26,580,000
2013	1359.456	48,037	65,300,000
Total	5595.268	516,942	318,980,000

The Renewable Fuel Standard (RFS) program regulations were expanded under the Energy Independence and Security Act (EISA) of 2007 which was developed by The U.S. Environmental Protection Agency (EPA) to ensure that there is a minimum volume of renewable fuels used for transportation in the United States. The requirement of Energy Independence and Security Act (EISA) of 2007 is four-fold increase in the volume of renewable fuels needed to be blended into conventional transportation fuels by 2022; from 9 billion gallons in 2008 to 36 billion gallons by 2022. Based on the projection of EIA in Annual Energy Outlook, Biodiesel production will be roughly constant in the upcoming

years to meet the current requirement of 1.28 billion gallons per year under the RFS (EPA, 2008; EIA, 2014a).

Table 6.9: Estimation of the resulted loss based on total risk for forecasted biodiesel production.

Estimation	US production, M gal	Average total risk, \$/M gal	Estimated loss, \$
as 2013	1360	64,618	87,880,000
as RFS	1280	64,618	82,711,000

6.2.3 Semi-quantitative Risk Matrix

Constructing the overall risk matrix of the biodiesel industry by taking both the transportation and the processing into account can be determined as a function of time by assessing the risk level in each year as illustrated in **Table. 6.10**. For the Biodiesel Plants, the risk matrix was constructed by analyzing each accident from the 58 total accidents happened and the corresponding risk levels falls in 4 regions (High, Serious, Medium, Eliminated). It can be concluded that 38% from the total plant accidents are having “High” risk level which is Non-Acceptable and must be changed immediately.

Whereas, the risk matrix representation for the transportation of selected input chemicals and the product (diesel fuel is representing biodiesel) involves treating the total

accidents (ranging from 39 to 306) occurred in each year for each chemical as one event. Clearly this rough approximation is used to ease the yearly risk level determination which otherwise would take too much time and effort to be done for a total of 5,460 accidents for all chemicals.

Table 6.10: Overall risk matrix on annual basis of biodiesel industry based on life-cycle approach over the period between 2006 and 2013.

Chemical Year	Methanol	NaOH	H ₂ SO ₄	Biodiesel Plants				Diesel
2006	Medium	Serious	High	3, High				Serious
2007	Medium	Medium	High	2, High	1, Serious	2, Medium	3, Eliminated	High
2008	Medium	Serious	High	5, High	1, Serious	2, Medium	2, Eliminated	Serious
2009	Medium	Serious	High	7, High	2, Serious	3, Medium	2, Eliminated	Serious
2010	Medium	Medium	High	2, High	1, Serious	2, Medium		Serious
2011	Medium	High	High	1, High	3, Serious	2, Medium		Serious
2012	Medium	Serious	High	1, High		3, Medium		High
2013	Medium	Serious	High	1, High		6, Medium	1, Eliminated	Serious

7. CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

This research focused on investigating the risk throughout the life cycle of the biodiesel industry in the United States. In order to achieve this goal, a holistic approach is proposed to assess the risk in both quantitative and semi-quantitative manners. The historical records of the reported accidents/incidents over the period of eight years, from 2006 until 2013, were utilized to quantify the risks based on actual incidents.

Based on the results obtained in this study, the following conclusions can be drawn:

- 1- In biodiesel plant accidents, a fire (whether alone or accompanied with spill or explosion) represents the most likely scenario for an accident (accounting for around 84.5% of the total accidents). The highest calculated probability is for Fire only type followed by Fire and Explosion one. Spill only or Explosion only types are much less probable to happen because they usually result in a fire due to the un-confinement of flammable chemicals involved in the process.
- 2- Most of the incidents/accidents were reported in biodiesel plants occurred in the process area, with a percentage of 43% of the total number, followed by the storage area, with a percentage of 33%.
- 3- For the storage accidents in the US biodiesel facilities, methanol (a main reactant) comes after the final product (biodiesel) as the main chemical leading to

incidents/accidents. Sulfuric acid contributed around 21% of the storage accidents and biomass, vegetable oil, only resulted in one accident.

- 4- According to the biodiesel risk matrix representation between 2006 and 2013 for biodiesel plants, 36% of the accidents were not acceptable and need immediate change, 14% require medium notice and additional safety measures while 40% need further action based on ALARP principle.
- 5- For plant accidents that address input chemicals storage, processing area, and product storage, there was a decrease in the risk per amount of production per year within the time period from 2006 till 2007 followed by an increase till 2009. Afterwards, the risk showed a decreasing profile until 2013 which indicates an improvement in the implementation of safety regulation and precautions in the US biodiesel plants.
- 6- In biodiesel transportation accidents, focus was given to a dominant biodiesel process (alkali-catalyzed transesterification). Methanol, sodium hydroxide and sulfuric acid were selected as the input chemicals. Selecting diesel fuel as a good representative for biodiesel was done because of data found available were very limited on the transportation of biodiesel itself.
- 7- The highway transportation mode is the dominant transportation mode that involves accidents while a slight contribution of the railways is observed especially in the transportation of sulfuric acid. Also, unloading the chemicals is the dominant phase in which the majority of the accidents occurred followed by the loading and transferring the chemicals.

- 8- The spillage comprises 97-98% of the events in the transportation accidents of each of the three selected chemicals. Also, when excluding the spillage, the dominant event type was vapor gas dispersion in methanol and sulfuric acid accidents.
- 9- By analyzing the causes of failure in the transportation accidents, it was found that the common causes included: dropping the chemical, failure of a component, improper or inadequate preparation for the transportation, overfilling, over pressuring, and human error.
- 10- Risk per amount of methanol transported (\$/ M gal methanol) reached the peak at 2009 then 2011 while risk as \$/ M lb NaOH was the maximum in 2013 then 2011. For sulfuric acid, 2011 had the highest risk (\$/ M gal H₂SO₄) followed by 2007. The value for risk of diesel (\$/ M gal diesel) was the greatest in 2011 then in 2006.
- 11- According to the biodiesel transportation risk matrix, sulfuric acid showed the highest level of risk, “High”, in all years even more than diesel fuel that exhibited “High” in 2 years and “Serious” in 6 years. Sodium hydroxide resulted in “High” in only one year, “Serious” in 5 years and “Medium” in 2 years whereas methanol, unexpectedly, had “Medium” risk level in all years.
- 12- From both phases of biodiesel industry (production plant and transportation), it was noticed that the transportation of the diesel fuel was associated with number of fatalities that is more than twice the number from the plant. The transportation of the selected input chemicals resulted in significant consequences which can be either very close to (for hospitalized) or exceed (for non-hospitalized) those that resulted from production plant. In addition, the cost of physical damage that resulted from the

transportation of the product was usually higher than what resulted from the plant accidents.

- 13- Total risk of biodiesel industry, \$/M gal biodiesel, based on life-cycle approach over the studied period showed that 2006 had the greatest value then the risk greatly declined in 2007 followed by an increase till 2009 then the risk declined again till 2012 then another increase was noticed in 2013.

7.2 Future Work

The current work can be extended in the following directions:

- 1- The current study focused on applying the holistic approach to determine the overall risk for biodiesel industry. Expansion in the type of product might be done by applying the same approach to address the risk involved in different biofuels production and comparing them from that perspective. Ethanol is a good candidate for the next study.
- 2- As mentioned before, several processes are used to produce biodiesel from different starting biomass feed stocks. Accordingly, significant number of input chemicals is utilized into these processes. For the sake of simplification, methanol, sodium hydroxide and sulfuric acid were selected to represent the alkali-catalyzed transesterification. Other input chemicals or production processes can be studied and compared as well.

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APPENDIX-A

Table A.1: Data used in the analysis in Chapter 3, (part 1/3).

Year	US Production, MM gallon	World Production, MM gallon	No. of Plants	No. of Accidents	No. of Accidents/plant	No. of States
2006	250	1710	86	3	0.035	3
2007	450	2775	165	8	0.048	8
2008	700	4232	171	10	0.058	9
2009	545	4699	173	14	0.081	12
2010	315	4893	100	5	0.05	5
2011	1100	5651	188	6	0.032	5
2012	1100	5670	180	4	0.022	4
2013	1800		155	8	0.052	8
Total	6260	29630	1218	58		54

Table A.2: Data used in the analysis in Chapter 3, (part 2/3).

Year	Event Location				Status		
	Storage	Process	Lauding / Unloading	No Info.	Operation	Maintenance	Shut Down
2006	2	0	1	0	3	0	0
2007	2	3	0	3	3	1	1
2008	4	3	1	2	3	2	3
2009	3	7	0	4	9	0	1
2010	3	1	0	1	4	0	0
2011	3	3	0	1	5	0	1
2012	0	3	0	0	4	0	0
2013	2	5	0	1	6	0	0
Total	19	25	2	12	37	3	6

Table A.3: Data used in the analysis in Chapter 3, (part 3/3).

Year	Consequences					
	Fatalities	Major Injuries	Minor Injuries	Major Damage	Minor Damage	total Damage
2006	1	1	1	3	0	3
2007	1	1	0	1	3	4
2008	2	4	4	4	3	7
2009	0	4	19	6	4	10
2010	0	2	3	2	3	5
2011	0	0	3	4	2	6
2012	1	0	2	1	2	3
2013	0	0	1	1	4	5
Total	5	12	33	22	21	43

Table A.4: Probability and severity levels of the investigated plant accidents.

Year	No. of Accidents	No. of Plants	Consequences					severity level	P(incident)/plant	probability level	Risk level
2006	3	86	Fatality	Major Injury	Minor Injury	Major Damage	Minor Damage	Critical	0.035	probable	High
			0	0	0	1	0	Critical	0.035	probable	High
			1	1	1	1	0	Catastrophic	0.035	probable	High
2007	8	165	0	0	0	0	0	0	0.05	probable	No data
			0	0	0	0	0	0	0.05	probable	No data
			0	0	0	0	1	Marginal	0.05	probable	Serious
			0	0	0	0	1	Negligible	0.05	probable	Medium
			1	0	0	1	0	Catastrophic	0.05	probable	High
			0	0	0	0	0	0	0.05	probable	No data
			0	0	0	0	1	Negligible	0.05	probable	Medium
			0	1	0	0	0	Catastrophic	0.05	probable	High
2008	10	171	0	3	1	1	0	Catastrophic	0.06	probable	High
			1	1	0	0	0	Catastrophic	0.06	probable	High
			1	0	1	0	1	Catastrophic	0.06	probable	High
			0	0	0	0	0	0	0.06	probable	No data
			0	0	0	1	0	Catastrophic	0.06	probable	High
			0	0	1	1	0	Marginal	0.06	probable	Serious
			0	0	0	1	0	Catastrophic	0.06	probable	High
			0	0	1	0	1	Negligible	0.06	probable	Medium
			0	0	1	0	1	Negligible	0.06	probable	Medium
			0	0	0	0	0	0	0.06	probable	No data

Year	No. of Accidents	No. of Plants	Consequences						severity level	P(incident)/plant	probability level	Risk level
			Fatality	Major Injury	Minor Injury	Major Damage	Minor Damage					
2009	14	173	0	0	0	0	1	Negligible	0.081	probable	Medium	
			0	0	0	0	1	Marginal	0.081	probable	Serious	
			0	0	0	0	1	Negligible	0.081	probable	Medium	
			0	1	0	0	0	Critical	0.081	probable	High	
			0	0	0	0	1	Marginal	0.081	probable	Serious	
			0	0	0	1	0	Critical	0.081	probable	High	
			0	0	0	0	0	0	0.081	probable	No data	
			0	0	0	1	0	Catastrophic	0.081	probable	High	
			0	2	19	1	0	Catastrophic	0.081	probable	High	
			0	0	0	0	0	0	0.081	probable	No data	
			0	0	0	1	0	Critical	0.081	probable	High	
			0	1	0	1	0	Critical	0.081	probable	High	
			0	0	0	0	0	Negligible	0.081	probable	Medium	
			0	0	0	1	0	Critical	0.081	probable	High	
2010	5	100	0	1	0	1	0	Critical	0.05	probable	High	
			0	1	2	0	1	Catastrophic	0.05	probable	High	
			0	0	0	0	1	Negligible	0.05	probable	Medium	
			0	0	1	1	0	Marginal	0.05	probable	Serious	
			0	0	0	0	1	Negligible	0.05	probable	Medium	
			0	0	0	0	1	Negligible	0.05	probable	Medium	
			0	0	0	0	1	Negligible	0.05	probable	Medium	
			0	0	0	0	1	Negligible	0.05	probable	Medium	

Year	No. of Accidents	No. of Plants	Consequences						severity level	P(incident)/plant	probability level	Risk level
2011	6	188	Fatality	Major Injury	Minor Injury	Major Damage	Minor Damage		Negligible	0.032	probable	Medium
			0	0	0	0	1		Marginal	0.032	probable	Serious
			0	0	0	1	0		Marginal	0.032	probable	Serious
			0	0	0	1	0		Marginal	0.032	probable	Serious
			0	0	1	1	0		Catastrophic	0.032	probable	High
			0	0	0	0	1		Negligible	0.032	probable	Medium
2012	4	180	0	0	0	0	1		Negligible	0.022	probable	Medium
			0	0	0	0	1		Negligible	0.022	probable	Medium
			0	0	1	0	0		Negligible	0.022	probable	Medium
			1	0	1	1	0		Catastrophic	0.022	probable	High
			0	0	0	0	1		Negligible	0.052	probable	Medium
2013	8	155	0	0	0	0	1		Negligible	0.052	probable	Medium
			0	0	0	0	1		Negligible	0.052	probable	Medium
			0	0	0	0	0		Negligible	0.052	probable	Medium
			0	0	1	0	1		Negligible	0.052	probable	Medium
			0	0	0	0	1		Negligible	0.052	probable	Medium
			0	0	0	0	0		0	0.052	probable	No data
			0	0	0	1	0		Catastrophic	0.052	probable	High
			0	0	0	0	0		Negligible	0.052	probable	Medium